Condensed Matter Physics

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Chapter-1: CRYSTAL STRUCTURE

• The solids are divided into two categories:

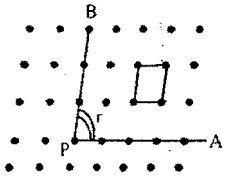
1. Amorphous solids
2. Crystalline solids.

Amorphous solids are those which lack the regular arrangement of atoms or moelcules and hence a short range order in their structure.

Crystalline solids are those which contain the regular repeated pattern of atoms or molecules and hence a long range order in their structure.

• **Lattice:** A lattice is defined as parallel net like arrangement of points provided the environment about any point is identical with environment about any other point.

Fig. below which is an array of points in two dimensions is called the plane lattice. If we extend this array of points in three dimensions then the array of points is called space lattice.

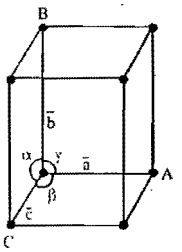


• **Translation operator:**

The position vector of any lattice point in three dimensions is expressed by the translational operator $\vec{T}$ given as $\vec{T} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$

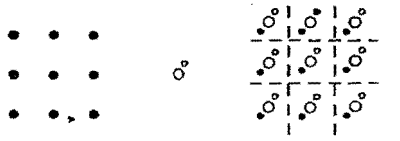
where n_1, n_2, n_3 are integral values which represent the number of lattice points along PA, PB and PC axes.

• **Unit cell:** The parallelopiped form by using the translations $\vec{a}, \vec{b}, \vec{c}$ as concurrent edges is called the unit cell.



• **Basis:** In the elementary crystals each lattice point of the lattice is occupied by an atom, while in the case of compounds each lattice point is occupied by an assembly of atoms which is repeated according to the translation vector $(\vec{T})$.

• **Crystal structure:**



• Crystal Systems:

There are 32 classes of Crystal systems based on geometrical considerations (i.e, symmetry and internal structure). But it is common practice to divide all Crystal systems into seven groups or basic systems.
The Basic Crystal system are:

(i) Cubic (ii) Tetragonal (iii) Orthorhombic (iv) Monoclinic (v) Triclinic

(vi) Trigonal (vii) Hexagonal

No.	Crystal class	Interception axes	Angles b/w axes	Types of Bravias space lattices.
1.	Cubic	a=b=c	$\alpha = \beta = \gamma = 90°$	Simple , BCC, FCC
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	Simple , BCC
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	Simple , BCC, FCC, Base centered
4.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	Simple , BCC
5.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$	Simple
6.	Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	Simple
7.	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	Simple

• Crystal Symmetry:

Operation that leaves the Crystal and its environment invariant.

(i) Operations performed about a point or a line are called point group symmetry.

(ii) Symmetry operation performed by translation as well are called space group.

• The different point group symmetry elements

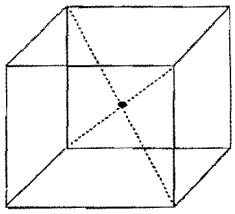
(i) Centre of symmetry or inversion centre.

(ii) Reflection symmetry

(iii) Rotation symmetry.

• Symmetry elements in a cubic Crystal:

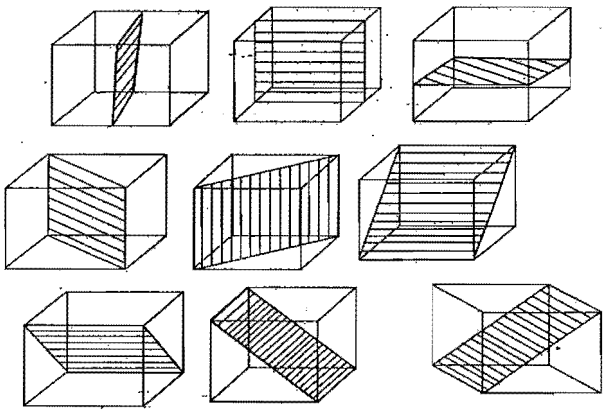
(i) Center of symmetry or Inversion centre:



A Crystal posses an inversion centre if for every lattice point given by the position vector $\bar{r}$ there will be corresponding lattice point at the position $-\bar{r}$.

Inversion is a symmetry operation in a Crystal equivalent to reflection through a point.

(ii) Reflection Symmetry:



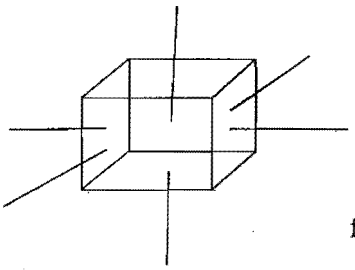
(iii) Rotational Symmetry:

If after rotation of the body about their axis by some angle Φ_n, the body appears as it did prior to rotation.

- Axis of symmetry may thus be defined as a line such that the Crystal assumes a congruent position. For every rotation of $\left[\frac{360}{n}\right]^\circ$, value of n decide the fold of the axis.

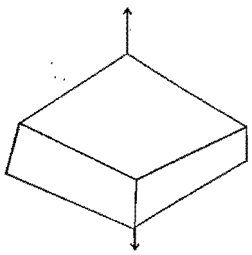
  Only one, two, three, four and six fold rotation axes of symmetry alone are possible in single Crystal.
- If a cube is rotated about a line perpendicular to one of its faces at its mid point, it will turn into a congruent position every 90°.

  Four times during a complete revolution.



four-fold symmetry.(tetrad axis)

Let the cube be now rotated about a solid diagram (Body diagonal) through 120° to get congruence, and such a line, of which there are four is therefore triad axis.



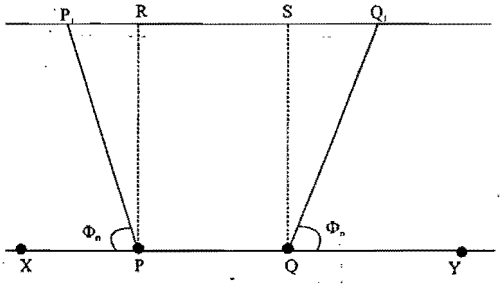
Finally, line joining the mid points of opposite parallel edges (diad axis)

Total no. of crystallographic symmetry elements of the cubic systems are thus

–Centre of symmetry	→1	$1 + 9 + 13 = 23$
–Straight planes	→3	
–Diagonal planes	→6	
–Tetrad axes	→3	
–Triad axes	→4	
–Diad axes	→6	

Example: To show that 5-fold rotation axis is not possible

Soln. Consider a lattice row XPQY



Let the lattice translation be 'a' and the lattice have n-fold rotation axis of symmetry.

Let us rotate the vectors PX and QY through an angle $\Phi_n = \left(\frac{360}{n}\right)^\circ$ in clockwise and anticlockwise direction.

The tips of the vectors P_1 and Q_1 in the new position must be lattice points if the lattice were to possess n-fold rotation axis of symmetry.

As per definition, rotation operation must be the lattice invariant. Clearly P_1Q_1 must be parallel to PQ and must be equal to an integeral multiple of the lattice translation 'a',

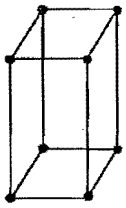
$P_1Q_1 = ma$ where m is an integer.

Thus, $\text{Cos}\Phi_n = \frac{P_1R}{PP_1}$ and $P_1R = PP_1\cos\Phi_n = a\cos\Phi_n$ and $SQ_1 = a\cos\Phi_n$ $\Rightarrow P_1Q_1 = P_1R + SQ_1 + RS$

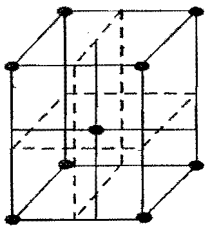
$\Rightarrow P_1Q_1 = 2a\cos\Phi_n + a = ma$, $1 + 2\cos\Phi_n = m$ $\Rightarrow 2\cos\Phi_n = m - 1 = N$ $\Rightarrow \cos\Phi_n = \left(\frac{m-1}{2}\right) = \frac{N}{2}$

N	N/2	$\cos\Phi_n$	Φ_n	N
–2	–1	–1	180°	2
–1	–1/2	–1/2	120°	3
0	0	0	90°	4
1	1/2	1/2	60°	6
2	1	1	360°	1

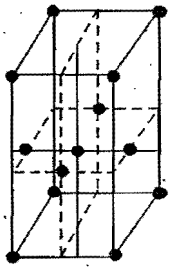
• **Cubic crystals:**



(a) Simple cubic
sc



(b) Body centred cubic unit cell.
bcc



(c) face centred cubic (fcc)

• **Co-ordination number:**

The coordination number is the number of nearest neighbours to a given atom in crystal lattice. Here we shall calculate the coordination number for simple cubic, bcc and fcc lattices.

(i) sc lattice:

In this lattice there is one atom at each of the eight corners of the cube. The atoms nearest to that at origin have, therefore, coordinates $(\pm a, 0, 0)$, $(0, \pm a, 0)$, $(0, 0 \pm, a)$; their number is obviously six hence the coordination number of a sc lattice is 6. The distance between two nearest atom is a.

Atomic radius (r) in this case $= \frac{a}{2}$.

(ii) bcc lattice:

In this lattice there is one atom at each of eight corners of the cube and one atom is at the body centre taking the central atom as the origin, the positions of neighbours are $\left(\pm\frac{a}{2}\hat{i} \pm\frac{a}{2}\hat{i} \pm\frac{a}{2}\hat{k}\right)$. Hence the coordination number of bcc lattice is 8. The distance between the two nearest neighbours is

$$\sqrt{\left(\frac{a}{2}\right)^2+\left(\frac{a}{2}\right)^2+\left(\frac{a}{2}\right)^2} = \frac{a\sqrt{3}}{2}\text{(half the diagonal)}$$

$$\text{atomic radius} = r = {}^{a\sqrt{3}}/_{4}$$

(iii) fcc lattice:

In this lattice there is one atom at each the eight corners of the cube and one at the centre of each of six faces of the cube. Taking any of the lattice point (atom) at the origin, the positions of nearest neighbours are

$$\left(\pm\frac{a}{2}\hat{i}\pm\frac{a}{2}\hat{j}\right),\left(\pm\frac{a}{2}\hat{j}\pm\frac{a}{2}\hat{k}\right),\left(\pm\frac{a}{2}\hat{k}\pm\frac{a}{2}\hat{i}\right)$$

Hence the coordination number of fcc lattice is 12. The distance between two nearest neighbours (of the same kind of ions) $= \sqrt{\left(\frac{a}{2}\right)^2+\left(\frac{a}{2}\right)^2+0^2} = \frac{a}{\sqrt{2}}$

$$\text{Atomic radius } r = \frac{a}{2\sqrt{2}}$$

Number of atoms per unit cell:

(i) sc lattice: Each ion forming a cubic lattice is a member of 8 cells. Thus the number of atoms per unit cell

bcc: $\frac{8}{8}=1$.

(ii) bcc lattice: Number of atoms per unit cell $=\frac{8}{8}+1=2$

(iii) fcc lattice: Number of atoms per unit cell is $\frac{8}{8}+\frac{6}{2}=1+3=4$

Example: Show that lattice constant 'a' in a cubic crystal is given by $a=\left(\frac{nM}{N\rho}\right)^{1/3}$

Soln. Volume of unit cell $= a^3$.

Mass of each unit cell $= a^3\rho$ ... (1)

If M is the molecular weight and N is the Avogadro number.

$\therefore$ Mass of each molecule $=\frac{M}{N}$

As if n is the number of molecules per unit cell, then the mass in each unit cell $= n.\frac{M}{N}$ ... (2)

From (1) and (2)

$$a^3\rho = n\frac{M}{N} \quad \Rightarrow \quad a=\left(\frac{nM}{N\rho}\right)^{1/3}$$

• Examples of sc, bcc and fcc:

sc → CsCl, CsBr

bcc → Li, Na, K, Cr

fcc → NaCl, diamond, Cu, Al, Ag.

• Packing fraction (f): Packing fraction (f) is defined as the ratio of volume (v) occupied by the atoms in a unit cell to that of the volume of the unit cell (V).

$$\Rightarrow \quad f=\frac{v}{V}=\frac{n.\frac{4}{3}.\pi r^3}{V}, \text{ n = number of atoms in the unitcell.}$$

(i) sc lattice: $PF=\frac{v}{V}=\frac{4}{3}\frac{\pi r^3}{a^3}=\left[\frac{4}{3}\right]\frac{(\pi r^3)}{8r^3}=\frac{\pi}{6}=0.52 \Rightarrow 52\%$

(ii) bcc lattice: $PF=\frac{v}{V}=\frac{8}{3}\frac{\pi r^3 3\sqrt{3}}{64r^3}=\frac{\sqrt{3}\pi}{8}=0.68 \Rightarrow 68\%$

(iii) fcc lattice: $PF=\left(\frac{16}{3}\right)\frac{\pi r^3 2\sqrt{3}}{64r^3}=\frac{\sqrt{2}\pi}{6}=\frac{\pi}{3\sqrt{2}}=0.74 \Rightarrow 74\%$

• **Second nearest neighbour distance:**

For sc second nearest neighbours distance $= a\sqrt{2}$

For bcc second nearest neighbours distance =a

For fcc second nearest neighbours distance = a

• **There are fourteen Bravais lattices and seven crystal systems.**

• **Interplanar spacing:** The spacing (or distance between two consecutive parallel planes (having same miller indices h, k, *l*) is given as $d_{h,k,\ell} = \dfrac{1}{\sqrt{\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{\ell^2}{c^2}}}$

If a = b = c(cubic crystal)= lattice constant (in Å)

$$\Rightarrow \quad d_{hk\ell} = \frac{a}{h^2 + k^2 + \ell^2}$$

• **Atomic density:** (No. of atoms per unit area of a lattice plane).

Atomic density $(\rho) = \dfrac{nd}{V}$, where V = volume of unit cell and n is the number of atoms in it and d is the interplanar spacing.

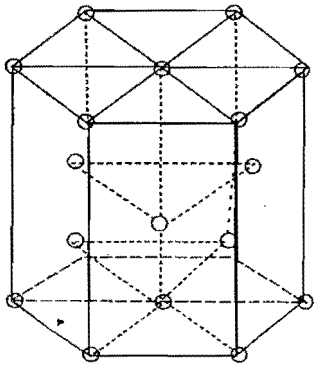
$$\therefore \quad \rho = \frac{nd}{abc}$$

If $n = 1 \quad \Rightarrow \quad \boxed{\rho = \dfrac{d}{abc}}$

• **Hexagonal close packed (hcp) structure:**

The specific hexagonal structure formed by magnesium is shown in figure. The unit cell contains one atom at each corner, one atom each at the centre of the hexagonal faces and three more atoms within the body of the cell. Each atom tocuhes three atoms in the layer below its plane, and three atoms in the layer above. Hence the coordination number of this structure is 12. Further the atoms touch each other along the edge of the hexagon. Thus, a = 2r.

The top layer contains seven atoms. Each corner atom is shared by 6 surrounding hexagon cells and the centre atom is shared by 2 surrounding cells. The three atoms within the body of the cell are fully contributing to the cell.



Thus, the total number of atoms in a unit cell is $\frac{3}{2}+\frac{3}{2}+3=6$

Calculation of $\left[\frac{c}{a}\right]$ ratio for an ideal hexagonal close packed structure. Let 'c' be the height of the unit cell and 'a' equilateral triangles at the top or base of the hexagonal cell. These three atoms just rest on the three atoms at the corners of the triangles.

In the triangle ABY, $\cos 30^\circ = \frac{AY}{AB}$

$$AY = a\cos 30^\circ = \frac{a\sqrt{3}}{2} \text{ and } (AZ)^2 = (AX)^2 + (ZX)^2$$

In triangle AXZ,

But, $$AX = \frac{2}{3}AY = \frac{2a}{3}\frac{\sqrt{3}}{2} = \frac{a}{\sqrt{3}}$$

Substituting this in equation ( )

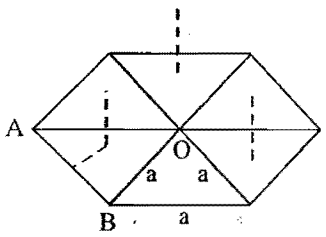
$$a^2 = \frac{a^2}{3}+\frac{c^2}{4}, \frac{c^2}{4} = a^2 - \frac{a^2}{3} = \frac{2a^2}{3}, \frac{c^2}{a^2} = \frac{8}{3} \text{ or } \frac{c}{a} = \left[\frac{8}{3}\right]^{1/2}$$

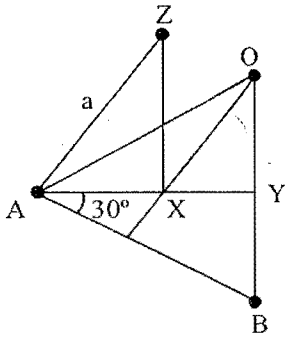
Volume of the unit cell:

Area of the base = Six times the area of the triangle AOB

Area of the triangle, $AOB = \frac{1}{2}(BO)(AY) = \frac{1}{2}a \times a\frac{\sqrt{3}}{2}$

Thus, area of the base $= 6 \times \frac{a^2}{2}\left[\frac{\sqrt{3}}{2}\right] = \frac{3}{2}\sqrt{3}\,a^2$





Volume of the cell, $V = \frac{3}{2}\sqrt{3}\,a^2c$

Calculation of packing factor of hcp:

Coordination number, N = 12; Lattice constant, a = 2r

Nearest neighbour distance, 2r = a; Number of atoms per unit cell, n = 6

Volume of all the atoms in a unit cell, $v = 6 \times \frac{4}{3}\pi r^3$; $v = \frac{24}{3}\pi\left[\frac{a}{2}\right]^3 = \pi a^3$

Volume of unit cell, $V = \frac{3}{2}\sqrt{3}\, a^2 c$ with $c/a = \left[\frac{8}{3}\right]^{1/2}$

Packing factor, (APF) = v/V

$$APF = \frac{\pi a^3}{\frac{3}{2}\sqrt{3}\, a^2 c} = \frac{2\pi}{3\sqrt{3}}\left(\frac{a}{c}\right) = \frac{2\pi}{3\sqrt{3}}\left[\frac{3}{8}\right]^{1/2} = \frac{\sqrt{2}\pi}{6} = \frac{\pi}{3\sqrt{2}} = \frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%$$

Magnesium, zinc, and cadmium crystalline in this structure. The packing factor of fcc and hcp are 74% and hence they are known as closest packing structures.

Diamond Cubic Structure:

The diamond lattice can be considered to be formed by interpenetrating two fcc lattices along the body diagonal by (1/4)th cube edge. One sublattice has its origin at the point (0, 0, 0) and the other at a point quarter of the way along the body diagonal (at the point a/4, a/4, a/4). The basic diamond lattice and the atomic positions in the cubic cell of diamond lattice and the atomic positions in the cubic cell of dimaond projected on a cube face are shown in figure. The fractions denote height about the base in units of cube edge. The point at 0 and 1/2 are on the fcc lattice, those at 1/4 and 3/4 are on a similar lattice displaced among the body diagonal by 1/4 of the cube edge.

The packing factor of this structure is thus calculated as follows:

$$(XY)^2 = \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 = \frac{a^2}{8}$$

$$(XZ)^2 = (XY)^2 + (YZ)^2 = \frac{a^2}{8} + \frac{a^2}{16} = \frac{3a^2}{16}$$

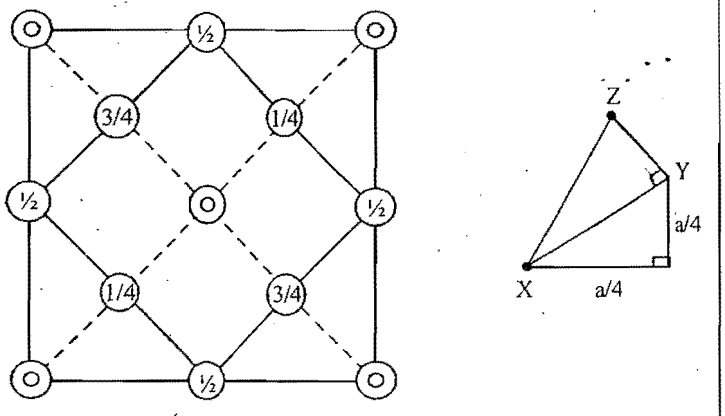


Figure: Diamond structure

But, $XZ = 2r$

Therefore, $(2r)^2 = \frac{3a^2}{16}$

(or) the nearest neighbour distance, $2r = \frac{\sqrt{3}a}{4}$

Lattice constant, $a = \frac{8r}{\sqrt{3}}$

$$\text{Packing factor} = v/V = \frac{8 \times \frac{4}{3}\pi r^3}{a^3} = \frac{32\,\pi r^3 3\sqrt{3}}{3\,(8r)^3} = \frac{\pi\sqrt{3}}{16} = 0.34 \text{ or } 34\%$$

Thus it is a loosely packed structure. Carbon, silicon and germanium crystalline in this structure.

Cubic Zinc sulphide or zinc blende structure:

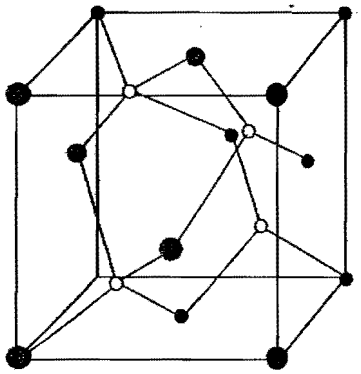


Figure: Zinc blende structure

Zinc blende structure is almost identical to the diamond structure except that the two interpenetrating fcc sublattices are of different atoms and displaced from each other by one-quarter of the body diagonal.

The cubic zinc sulphide structure results when zinc atoms are placed on one fcc lattice and S atoms on the other fcc lattice as shown in figure. The conventional cell of this structure is a cube. There are four molecules per conventional cell. For each atom, there are four equally distant atoms of opposite kind arranged at a regular tetrahedron. The compounds which have cubic zinc sulphide structure are CuCl, ZnS, InSb and CdS.

• Sodium chloride structure:

In sodium chloride, sodium loses its outer electron and acquires an excess of positive charge while the chlorine atom accepts one electron from sodium and becomes a negative ion. Now, due to the electrostatic forces between the excess charges, the two ions attract each other. Further, due to the strong forces of repulsion as their outer electron shells come into close proximity, the two ions cannot approach each other to within less than certain distance. When attraction and repulsion balance, equilibrium is obtained. The Bravais lattice is a face centred cube, with a basis of one Na ion and one Cl ion separated by one-half the body diagonal of the unit cell. There are four molecules of NaCl in a unit cell, with ions in the positions.

$$\text{Na}: \frac{1}{2}\frac{1}{2}\frac{1}{2};\ 0\ 0\ \frac{1}{2};\ 0\ \frac{1}{2}\ 0;\ \frac{1}{2}\ 0\ 0$$

$$\text{Cl}: 0\ 0\ 0;\ \frac{1}{2}\ \frac{1}{2}\ 0;\ \frac{1}{2}\ 0\ \frac{1}{2};\ 0\ \frac{1}{2}\ \frac{1}{2}$$

In this structure, each ion is surrounded by six nearest neighbours of the opposite kind. The coordination number is therefore six. There are twelve next nearest neighbours of the same kind as the reference ion. Representative crystals having NaCl structure are KCl, KBr, MgO, AgBr, etc.

• Caesium Chloride structure:

CsCl structure is showin figure ( ).

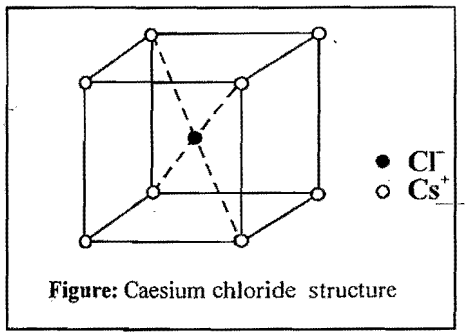


Figure: Caesium chloride structure

The space lattice.is simple cubic. The basis has one Cs+ ion at 0 0 0 and one Cl⁻ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

Each ion is at the centre of a cube of ions of the opposite kind, the coordination number is thus eight. Obviously, the lattice points of CsCl are two interpenetrating simple cubic lattices, the corner of one sublattice is the body centre of the other. One sublattice is occupied by Cs+ ions and the other by Cl– ions. CsCl, RbCl and LiHg are some materials crystallizing in this structure.

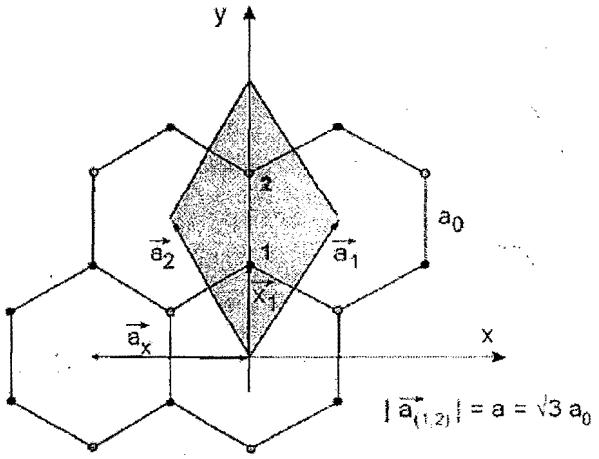
• Wigner Seitz Unit cell (Hexagon in this case):

• a_1 and a_2 are the primitive vectors of the graphene unit cell.

• Area of the unit cell will be $\sqrt{3}\, a^2/2$. where a is the lattice parameter.

• a_0 shown in the figure is nearest-neighbour distance but not lattice parameter .

• Bravais lattice of graphene is either hexagonal or triangular with basis as shown previously.



$\vec{a}_1 = a_0\sqrt{3}\,(1/2, \sqrt{3}/2)$

$\vec{a}_2 = a_0\sqrt{3}\,(-1/2, \sqrt{3}/2)$

• Milller Indices:

Crystal lattice may be regarded as made up of an aggregate of a set of parallel equidistant planes passing through the lattice points are called lattice planes. Millier indices is a method to designate such plane.

(i) Determine the coordinates of the intercepts made by the plane along the three crystallographic axes (x, y, z axes).

x	y	z
2a	3b	c
pa	qb	rc (p = 2, q = 3 cad r = 1)

(ii) Express the intercepts as multiples of the unit cell dimensions or lattice parameter along the axes i.e.,

$$\frac{2a}{a}, \frac{3b}{b}, \frac{c}{c}$$

$$2 \quad 3 \quad 1$$

(iii) Determine the reciprocals of these no's 1/2, 1/3, 1/1

(iv) Reduce these reciprocals to the smallest set of integral no's and enclose then in bracket.

$$6\times\frac{1}{2}, \quad 6\times\frac{1}{3}, \quad 6\times 1$$

$$(3 \qquad 2 \qquad 6)$$

This is (h k *l*)

Miller indices may be defined as the reciprocals of the intercepts made by plane on the cyrstallographic axes when reduces to smallest no's.

Example: Calculate the lattice constant of NaCl Crystal . The density of NaCl is 2189 kg/m^3 and Avogadro's no N is 6.02×10^{26} /kg – molecule

Soln: Fcc lattice $a = \left(\frac{nM}{NP}\right)^{1/3}$

M(NaCl) = 58.5 kg / kg- molecule (or gm/gm mol)

n = 4

$$\therefore a = \left[\frac{4\times 58.5}{6.02\times 10^{26}\times 2189}\right] = \left(177\times 10^{-30}\right)^{1/3} = 5.61 \times 10^{-10}\ \text{m} = 5.61\text{Å}$$

Example: Find the ratio of intercepts on the three axes by $(1\bar{3}\,2)$ planes in simple cubic lattice.

Soln. Let p, q, r be the intercepts on the x, y and z axis respectively. Then

$$p : q : r = \frac{a}{h} : \frac{b}{k} : \frac{c}{l}$$

$$p : q : r = \frac{a}{1} : \frac{a}{-3} : \frac{a}{2} = 6 : -2 : 3$$

Example: In a tetragonal lattice a = b = 2.5 Å c = 1.8 Å. Deduce the lattice spacing between (1 1 1) planes.

Soln. $$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}} = 1.26\ \text{Å}$$

Example: For a simple cubic crystal find (i) the ratio of intercepts on the three axe by (1 2 3) plane, (ii) the ratio of the spacings of (1 1 0) and (1 1 1) plane and (iii) the ratio of nearest neighbour distance to the next nearest neighbour distance.

Soln. (i) $p:q:r=\frac{a}{h}:\frac{b}{k}:\frac{c}{l}$

$p:q:r=\frac{a}{1}:\frac{a}{2}:\frac{a}{3}=6:3:2$

(ii) $d_{hkl}=\frac{a}{\sqrt{h^2+k^2+l^2}}$ $\quad d_{110}=a/\sqrt{2}$ $\quad\Rightarrow d_{111}=a/\sqrt{3}$ $\quad\therefore \frac{d_{110}}{d_{111}}=\sqrt{3}:\sqrt{2}$

(iii) In a simple cubic, distance b/w nearest neighbour is a and that b/w next nearest neighbour is $\sqrt{2}a$

Their ratio $=\frac{a}{\sqrt{2}a}=1:\sqrt{2}$.

Exmaple: Calculate the density of (1 0 0) plane in a simple cubic (p) lattice; given a = 2.5 Å.

Soln. $\rho=\frac{d}{a^3}$ $\quad$ Now $d_{100}=a$

$\Rightarrow \rho=\frac{a}{a^3}=\frac{1}{a^2}=\frac{1}{\left(2.5\times10^{-10}m\right)^2}=1.6\times10^{19}$

Example: Compare the densities of lattice points in (1 1 1) and (1 1 0) planes in an simple cubic lattice.

Soln. $\rho=\frac{d}{abc}=\frac{d}{a^3}\Rightarrow\frac{\rho_{111}}{\rho_{110}}=\frac{d_{111}}{d_{110}}\quad\Rightarrow\frac{\rho_{111}}{\rho_{110}}=\frac{a/\sqrt{3}}{a/\sqrt{2}}=\frac{\sqrt{2}}{\sqrt{3}}$

Exmaple: Sodium transform from B.C.C to H.C.P. crystal structure at 23° K without change of density in the cubic face a = 4.23Å and in bcp face $\frac{c}{a}=1.63$. Find lattice constant in hcp face.

Soln. Volume of hcp cell $=\frac{3\sqrt{3}}{2}a^2c$.

Volume of bcc cell $=a^3$.

mass = volume × density

$\Rightarrow$ Volume of bcc = Volume of hcp

$\frac{3\sqrt{3}}{2}a_2^2c=a_1^3$ $\qquad\frac{c}{a_2}=1.63$

$\frac{3\sqrt{3}}{2}\times a_2^3(1.63)=a_1^3,\ c=1.63a_2\quad\Rightarrow\frac{3\sqrt{3}}{2}\times a_2^3(1.63)=(4.23)^3$

$a_2=\left(\frac{(4.23)^3\times2}{3\times1.732\times1.63}\right)^{\frac{1}{3}}\quad\Rightarrow a_2=2.6144Å$

Example: Find the Miller indices for planes in each of the following sets which intercepts $\bar{a}$, $\bar{b}$ and $\bar{c}$ at (i) 3a, 3b, 2c ; (ii) a, 2b, ∞ ; (iii) a, b / 2, c , (iii) 3a, 2b, 2c

Soln. (i) Set of intercepts = 3a, 3b, 2c

Reciprocal of numbers representing the intercepts are $\frac{1}{3},\frac{1}{3},\frac{1}{2}$

Smallest three integers having the same ratio are 2, 2, 3.

Therefore, Miller indices are = (2 2 3)

(ii) Set of intercepts are a, 2b, ∞

Reciprocals of numbers are $1, \frac{1}{2}, 0$

Smallest three integers having the same ratio, 2, 1, 0
Therefore, Miller indices are (2 1 0)

(iii) Set of intercepts = $a, \frac{b}{2}, c$

Reciprocal of numbers are 1, 2, 1
Therefore, Miller indices are (1 2 1)
(iv) Sets of intercepts are 3a, 2b, 2c

Reciprocals of numbers representing the intercepts are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$

Smallest three integers having the same ratio are 2, 3, 3.
Therefore, Miller indices are (2 3 3).

Example: Calculate the separation between lattice planets in a simple cubic, face centred cubic (fcc) and body centred cubic (bcc) lattice.

Soln. Simple cubic lattice (sc). A simple cubic lattice has (1 0 0), (1 1 0) and (1 1 1) planes. The (1 0 0) planes cut the X-axis and are parallel to Y and Z-axis.

$$\Rightarrow \qquad d_{100} = \frac{a}{\left[1^2+0+0\right]^{1/2}} = a$$

The (1 1 0) planes cut obliquely across X and Y axis but are parallel to Z-axis.

$$\Rightarrow \qquad d_{110} = \frac{a}{\left[1^2+1^2+0\right]^{1/2}} = \frac{a}{\sqrt{2}}$$

Face centred cubic lattice: In fcc lattice there is one unit situated at each corner and one unit at the centre of each of the six faces. Thus an additional (1 0 0) plane arises half way between the (1 0 0) planes. These additional planes pass through the centre of the front and back face. As the distance between (1 0 0) planes of a simple cubic lattice is a, the distance between (100) planes of the fcc lattice is $\frac{a}{2}$.

$$\Rightarrow \qquad d_{100} = \frac{1}{2}a$$

Similarly, there arises are an additional set of (1 1 0) planes parallel to the first set midway between the planes of simple cubic lattice.

$$\Rightarrow \qquad d_{110} = \frac{1}{2}\frac{a}{\sqrt{2}}$$

The (1 1 1) planes of simple cubic lattice pass through the centre of all the faces of fcc lattice and hence no new planes arise in this case.

$$\Rightarrow \qquad d_{111} = \frac{a}{\sqrt{3}}$$

Body centred cubic lattice: In bcc lattice one unit is situated at each corner and one at the centre of the cubic. An additional (1 0 0) plane arises half way between (1 0 0) planes of a simple cubic frame.

$$\Rightarrow \qquad d_{100} = \frac{1}{2}a$$

The (1 1 0) plane is the same as in a simple lattice.

$$\Rightarrow \qquad d_{110} = \frac{1}{2}\frac{a}{\sqrt{2}}$$

The (1 1 1) plane of a bcc lattice lies midway between the (1 1 1) planes of a simple cubic lattice.

$$\Rightarrow \qquad d_{111} = \frac{1}{2}\frac{a}{\sqrt{3}}$$

Example: Find the Miller indices of a set of parallel planes which make intercepts in the ratio of 2a : 3b on the X and Y axis and are parallel to Z-axis; $\vec{a}, \vec{b}, \vec{c}$ being primitive vectors of the lattice. Also calculate the interplanar distance 'd' of the planes taking the lattice to be a cube with a = b = c = 3Å.

Soln. Intercepts on the X-axis = 2a
Intercept on the Y-axis = 3b
Intercept on the Z-axis $= \infty$ As the set of planes is parallel to Z-axis.

The reciprocals of the numbers 2, 3 and ∞ are $\frac{1}{2}, \frac{1}{3}, \frac{1}{\infty}$ or zero.

The smallest three integers having the same ratio are 3, 2, 0
Therefore, Miller indices (h k l) = (3 2 0)
Lattice constant a = b = c = 3Å

Therefore, interplanar distance $d = \frac{a}{\sqrt{h^2 + k^2 + \ell^2}} = \frac{3Å}{\sqrt{3^2 + 2^2 + 0^2}} = \frac{3}{\sqrt{13}}Å$

SUMMARY

1. The solids may be broadly classified as crystalline and non-crystalline (or amorphous). The crystalline solids may be further sub-divided into single crystals and polycrystalline materials.

2. Crystallography is the study of formation, structure and properties of crystals.

3. A crystal structure results from the combination of a space lattice and a basis. A space lattice is a regular arrangement of infinite number of imaginary points in three-dimensional space. A basis is a structural unit comprising a single atom or a group of atoms which is placed on each lattice point in a regular fashion to generate the crystal structure.

4. A unit cell is a small group of points which acts as a building block for the entire latice. It may be primitive or non-primitive. A primitive cell is the smallest volume unit cell and contains only one lattice point per cell. A non-primitive cell contains more than one lattice points per cell. The conventional unit cell has the highest possible symmetry and the lowest possible volume. It may be primitive or non-primitive.

5. The effective number of lattice points belonging to a unit cell is

$$N = N_i + N_f/2 + N_c/8$$

where N_i, N_f and N_c denote the number of lattice points present inside, at the face centres, and at the corners of the cell respectively.

6. A crystal remains invariant under the application of various symmetry operations like translation, rotation, reflection, inversion etc. Some rotational operations, such as 5-fold and 7-fold rotations, are not permissible as these are not compatible with lattice translation symmetry.

7. A point group is the combination of certain symmetry operations like rotation, reflection and inversion. It determines the symmetry of space around a point. The number of point groups in three-dimensional space is 32. These point groups produce only 14 Bravais lattices.

8. The set of all the symmetry elements of a crystal structure is called the space group. The number of distinct space groups possible in three dimensions is 230.

9. The Miller indices of a crystallographic plane and a direction are denoted by (hkl) and $[h'k'\ell']$ respectivley where h, k and l are integers. The parallel planes have the same indices.

10. The angle between two directions [hkl] and $[h'k'l']$ is given by

$$\cos\theta = \frac{hh' + kk' + \ell\ell'}{\left(h^2 + k^2 + \ell^2\right)^{1/2}\left(h'^2 + k'^2 + \ell'^2\right)^{1/2}}$$

11. The interplanar distance for the paralle (hkl) planes for an orthoorhombic lattice is

$$d = \left(h^2/a^2 + k^2/b^2 + \ell^2/c^2\right)^{-1/2}$$

where a, b and c are the lengths of the axes.

12. A close-packed structure is that in which each atom has twelve indentical nearest neighbours. A close-packed structure may be either fcc or hcp with the following sequence of layers:

hcp: .....ABABABAB.....

fcc: .....ABCABCABC.....

Chapter-2: RECIPROCAL LATTICE & X-RAY DIFFRACTION

• Reciprocal lattice:

Every crystal has two lattices associated with it, the crystal lattice (or direct space lattice) and the reciprocal lattice.

The concept of reciprocal lattice was devised for the purpose of tabulating two important properties of crystal planes; their slope and their interplanar spacing.

Each set of parallel planes in a direct lattice can be represented by a normal to these planes having length equal to the reciprocal of the interplanar spacing. The normals are drawn with reference to any arbitrary origin and points are marked at their ends. These points form a regular arrangement which is called reciprocal lattice. Thus each point in a reciprocal lattice is a representative point of a particular parallel to set of planes. It is easier to deal with such points than to deal with set of planes. This is why we use reciprocal lattice.

Thus reciprocal lattice vector is a vector whose magnitude is equal to the reciprocal of the inter planar spacing i.e., $\frac{1}{d_{hk\ell}}$ and direction is parallel to the normal to (hk*l*) plane.

Why reciprocal lattice is so named? The reciprocal lattice is so named because the length assigned to each normal representing the reciprocal lattice is proportional to the reciprocal of the interplanar spacing of that plane in ordinary space.

• Primitive translation vectors of reciprocal lattice:

Let $\vec{a}, \vec{b}, \vec{c}$ be the primitive translation vectors of a direct space lattice for a crystal forming a primitive unit cell. The volume of this unit cell is given by

$$V = \vec{a}.\left(\vec{b}\times\vec{c}\right) = \vec{b}.\left(\vec{c}\times\vec{a}\right) = \vec{c}.\left(\vec{a}\times\vec{b}\right)$$

The vectors given by $\vec{A} = 2\pi\frac{\vec{b}\times\vec{c}}{\vec{a}.\left(\vec{b}\times\vec{c}\right)};\ \vec{B} = 2\pi\frac{\vec{c}\times\vec{a}}{\vec{b}.\left(\vec{c}\times\vec{a}\right)};\ \vec{C} = 2\pi\frac{\vec{a}\times\vec{b}}{\vec{c}.\left(\vec{a}\times\vec{b}\right)}$

are known as reciprocal lattice vectors or primitive translation vectors of reciprocal lattice.

$$\vec{A}.\vec{a} = 2\pi,\ \vec{A}.\vec{b} = 0 \text{ and } \vec{A}.\vec{c}=0$$

$$\Rightarrow \quad \vec{B}.\vec{a} = 0,\ \vec{B}.\vec{b} = 2\pi \text{ and } \vec{B}.\vec{c}=0$$

$$\Rightarrow \quad \vec{C}.\vec{a} = 0,\ \vec{C}.\vec{b} = 0 \text{ and } \vec{C}.\vec{c}=2\pi$$

Choosing $\vec{A}, \vec{B}$ and $\vec{C}$ as the primitive translation vectors of the reciprocal lattice (also known as reciprocal axes) we can construct the reciprocal lattice points or reciprocal lattice vectors given by

$$\vec{G} = h\vec{A} + k\vec{B} + \ell\vec{C}$$

where **hkl** are intergers and define the coordinate of the point in the reciprocal space.

The crystal lattice is a lattice in real or ordinary space whereas reciprocal lattice is a lattice in the reciprocal space or associated $\vec{k}$ space or Fourier space. The wave vector $\vec{k}$ is always drawn in Fourier space. Vectors in the crystal lattice have dimensions of length $\left[L^1\right]$ and vectors in the reciprocal lattice have dimensions of 1/Length (L^{-1}).

• Properties of reciprocal lattice:

(i) The direct lattice is the reciprocal lattice to its own reciprocal lattice. Simple cubic lattice is self reciprocal whereas bcc and fcc lattices are reciprocal of each other.

(ii) Each point in a reciprocal lattice corresponds to a particular set of parallel planes of the direct lattice.

(iii) The distance of a reciprocal lattice point from an arbitrarily fixed origin is inversely proportional to the interplanar spacing of the corresponding parallel planes of the direct lattice.

(iv) The unit cell of the reciprocal lattice is not necessarily a parallelopiped. We deal with the Wigner Seitz cell of the reciprocal lattice which constituents the Brillouin zone.

(v) The volume of a unit cell of the reciprocal lattice is inversely proportional to the volume of the corresponding unit cell of the direct lattice.

• sc lattice: Let the primitive translation vectors of a simple cubic cell be $\vec{a}$, $\vec{b}$ and $\vec{c}$. We can write the vectors as

$$\vec{a} = a\hat{x},\ \vec{b} = a\hat{y} \text{ and } \vec{c} = a\hat{z}$$

The primitive translation vectors of the reciprocal sc lattice are given by

$$\vec{A} = 2\pi\frac{\vec{b}\times\vec{c}}{\vec{a}.(\vec{b}\times\vec{c})} = 2\pi\frac{a\hat{y}\times a\hat{z}}{a^3} = \frac{2\pi}{a}\hat{x}\ ;\ \vec{B} = 2\pi\frac{\vec{c}\times\vec{a}}{\vec{b}.(\vec{c}\times\vec{a})} = 2\pi\frac{a\hat{z}\times a\hat{x}}{a^3} = \frac{2\pi}{a}\hat{y}$$

$$\vec{C} = 2\pi\frac{\vec{a}\times\vec{b}}{\vec{c}.(\vec{a}\times\vec{b})} = 2\pi\frac{a\hat{x}\times a\hat{y}}{a^3} = \frac{2\pi}{a}\hat{z}$$

$$\vec{a}' = \frac{a}{2}(\hat{x}+\hat{y}-\hat{z});\ \vec{b}' = \frac{a}{2}(-\hat{x}+\hat{y}+\hat{z});\ \vec{c}' = \frac{a}{2}(\hat{x}-\hat{y}+\hat{z})$$

• bcc lattice: The primitive translation vectors of the reciprocal bcc lattice are given by

$$\vec{A} = 2\pi\frac{\vec{b}'\times\vec{c}'}{\vec{a}'.(\vec{b}'\times\vec{c}')} = 2\pi\frac{\frac{a^2}{2}(\hat{x}+\hat{y})}{a^3/2} = \frac{2\pi}{a}(\hat{x}+\hat{y})$$

Similarly, $$\vec{B} = 2\pi\frac{\vec{c}'\times\vec{a}'}{\vec{b}'.(\vec{c}'\times\vec{a}')} = 2\pi\frac{\frac{a^2}{2}(\hat{y}+\hat{z})}{a^3/2} = \frac{2\pi}{a}(\hat{y}+\hat{z})$$

$$\vec{C} = 2\pi\frac{\vec{a}'\times\vec{b}'}{\vec{c}'.(\vec{a}'\times\vec{b}')} = 2\pi\frac{\frac{a^2}{2}(\hat{z}+\hat{x})}{a^3/2} = \frac{2\pi}{a}(\hat{z}+\hat{x})$$

$$\vec{a}' = \frac{a}{2}(\hat{x}+\hat{y});\ \vec{b}' = \frac{a}{2}(\hat{y}+\hat{z});\ \vec{c}' = \frac{a}{2}(\hat{z}+\hat{x})$$

• fcc lattice: The primitive translation vectors of the reciprocal fcc lattice are given by

$$\vec{A} = 2\pi\frac{\vec{b}'\times\vec{c}'}{\vec{a}'.(\vec{b}'\times\vec{c}')} = \frac{2\pi\frac{a^2}{4}(\hat{x}+\hat{y}-\hat{z})}{a^3/4} = \frac{2\pi}{a}(\hat{x}+\hat{y}-\hat{z})$$

Similarly, $$\vec{B} = \frac{2\pi}{a}(-\hat{x}+\hat{y}+\hat{z}) \text{ and } \vec{C} = \frac{2\pi}{a}(\hat{x}-\hat{y}+\hat{z})$$

Example: Two dimensional lattice has the basis vectors $\vec{a} = 2\hat{x}; \vec{b} = \hat{x} + 2\hat{y}$. Find the reciprocal lattice vectors.

Soln. This is a two dimensional problem. If we assume that the third dimensional lattice basis vector $\vec{c}$ is parallel to Z-axis i.e. $c = \hat{z}$, then we can use the three dimensional relation.

The plane of the reciprocal lattice vector $\vec{A}$ and $\vec{B}$ will be plane of basis vector $\vec{a}$ and $\vec{b}$.

Now, $\vec{A} = \dfrac{(\vec{b}\times\vec{c})}{\vec{a}.(\vec{b}\times\vec{c})}$ and $\vec{B} = \dfrac{(\vec{c}\times\vec{a})}{\vec{b}.(\vec{c}\times\vec{a})}$ $\Rightarrow$ $(\vec{b}\times\vec{c}) = (\hat{x}+2\hat{y})\times(\hat{z}) = -\hat{y}+2\hat{x}$

$\Rightarrow$ $(\vec{c}\times\vec{a}) = (\hat{z})\times(2\hat{x}) = 2\hat{y}$

$\Rightarrow$ $\vec{a}.(\vec{b}\times\vec{c}) = 2\hat{x}.(-\hat{y}+2\hat{x}) = 4$ and $\vec{b}.(\vec{c}\times\vec{a}) = (\hat{x}+2\hat{y}).2\hat{y} = 4$

$\vec{A} = \dfrac{-\hat{y}+2\hat{x}}{4} = \dfrac{1}{2}\hat{x} - \dfrac{1}{4}\hat{y}$ $\Rightarrow$ $\vec{B} = \dfrac{2\hat{y}}{4} = \dfrac{1}{2}\hat{y}$

These are the required reciprocal lattice verctors in two dimensions.

Example: The primitive translation vectors of a hexagonal space lattice are

$$\vec{a} = \left(\frac{a}{2}\right)\hat{x} + \left(\frac{1}{16}a\right)\hat{y}; \vec{b} = -\left(\frac{a}{2}\right)\hat{x} + \left(\frac{1}{16}a\right)\hat{y}; \vec{c} = c\hat{z}$$

Find (i) volume of the primitive cell and (ii) primitive translations of the reciprocal lattice.

Soln. (i) The volume V of the primitive cell is given by

$$V = \left[\vec{a}.(\vec{b}\times\vec{c})\right]$$

Now, $(\vec{b}\times\vec{c}) = \left[-\left(\dfrac{a}{2}\right)\hat{x} + \left(\dfrac{1}{16}a\right)\hat{y}\right]\times c\hat{z} = \left(\dfrac{ac}{2}\right)\hat{y} + \left(\dfrac{ac}{16}\right)\hat{x}$

$\Rightarrow$ $\vec{a}.(\vec{b}\times\vec{c}) = \left[\left(\dfrac{a}{2}\right)\hat{x} + \left(\dfrac{1}{16}a\right)\hat{y}\right].\left[\left(\dfrac{ac}{2}\right)\hat{y} + \left(\dfrac{ac}{16}\right)\hat{x}\right] = \dfrac{a^2c}{32} + \dfrac{a^2c}{32} = \dfrac{a^2c}{16}$

(ii) Let the primitive translations of reciprocal lattice be $\vec{A}$, $\vec{B}$ and $\vec{C}$, then

$$\vec{A} = 2\pi\frac{(\vec{b}\times\vec{c})}{\vec{a}.(\vec{b}\times\vec{c})}$$

Now, $(\vec{b}\times\vec{c}) = \left[\left(-\dfrac{a}{2}\right)\hat{x} + \left(\dfrac{a}{16}\right)\hat{y}\right]\times c\hat{z} = \dfrac{ac}{2}\hat{y} + \dfrac{ac}{16}\hat{x}$

Also, $\vec{a}.(\vec{b}\times\vec{c}) = \dfrac{a^2c}{16}$

$\Rightarrow$ $\vec{A} = 2\pi\dfrac{\dfrac{ac}{2}\hat{y} + \dfrac{ac}{16}\hat{x}}{\dfrac{a^2c}{16}} = \left(2\dfrac{\pi}{a}\right)\hat{x} + \left(\dfrac{16\pi}{a}\right)\hat{y}$

Again, $$\vec{B}=\frac{2\pi(\vec{c}\times\vec{a})}{\vec{b}.(\vec{c}\times\vec{a})}$$

Now, $$(\vec{c}\times\vec{a})=c\hat{z}\times\left[\left(\frac{a}{2}\right)\hat{x}+\left(\frac{a}{16}\hat{y}\right)\right]=\left(\frac{ac}{2}\right)\hat{y}-\left(\frac{ac}{16}\right)\hat{x}$$

$$\Rightarrow \quad \vec{B}=\frac{2\pi\left(\frac{ac}{2}\right)\hat{y}-\left(\frac{ac}{16}\right)\hat{x}}{\frac{\vec{a}\cdot\vec{c}}{16}}=-\left(\frac{2\pi}{a}\right)\hat{x}+\left(\frac{16\pi}{a}\right)\hat{y}$$

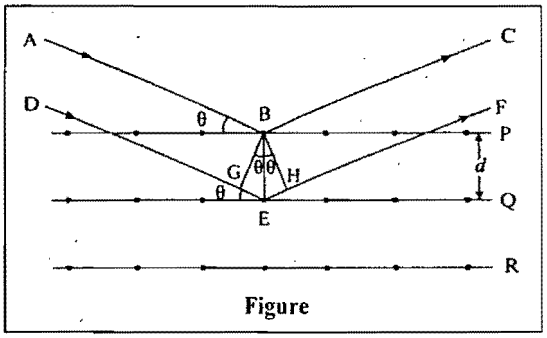
Similarly, $$\vec{C}=\frac{2\pi(\vec{a}\times\vec{b})}{\vec{c}.(\vec{a}\times\vec{b})}$$

Now, $$(\vec{a}\times\vec{b})=\left[\left(\frac{a}{2}\right)\hat{x}+\left(\frac{a}{16}\right)\hat{y}\right]\times\left[\left(-\frac{a}{2}\right)\hat{x}+\left(\frac{a}{16}\right)\hat{y}\right]=\left[\frac{a^2}{32}\right]\hat{z}+\left(\frac{a^2}{32}\right)\hat{z}=\frac{a^2}{16}\hat{z}$$

$$\Rightarrow \quad \vec{C}=\frac{2\pi\frac{a^2}{16}\hat{z}}{\frac{a^2c}{16}}=\left(\frac{2\pi}{c}\right)\hat{z}$$

•X-ray diffraction:

Consider parallel lattice planes equidistant from one another in a crystal structure, separated by a distance 'd'. Suppose a beam of X-rays AB of wavelength λ is incident on a layer of atoms in one cleavage plane P of a crystal at a glancing angle θ at B and after reflection goes along BC. The ray DE incident on cleavage plane Q after reflection goes along EF. Draw BG perpnendicular on DE and BH perpendicular on EF, then BG is the incident wave front and BH the reflected wave front.



Figure

Path difference between the two wave fronts = GE + EH

Now, in ΔBGE, $GE = BE\sin\theta = d\sin\theta$ and in ΔBEH, $EH = BE\sin\theta = d\sin\theta$

Therefore, Path-difference, $GE + EH = 2d\sin\theta$

If this path-difference is an integral multiple of wavelength λ, constructive interference will take place between the reflected beams. Thus the intensity will be maximum if

$$2d\sin\theta = n\lambda \qquad \text{where } n = 1, 2, 3, ...$$

For n = 1, we get the first order spectrum and for n = 2, we get the second order spectrum and so on. This phenomenon is similar to that of the optical diffraction with diffraction grating with only this difference that here vrious parallel planes of the crystal act as lines in the grating. The above equation $2d\sin\theta = n\lambda$ is Bragg's equation and represents Bragg's law.

• **Significance:** The interpretation of Bragg's law gives that the diffraction intensities can be stronger only at certain values of θ for specific values of λ and d. Therefore, a knowledge of experimentally observed diffraction angles and wavelength of X-rays can provide the information about the inter planar spacing of the crystal. Thus, the space, shape and orientation of the unit cell can be determined from any diffraction experiment using monochromatic X-rays.

Example: The spacing between successive (1 0 0) planes in NaCl is 2.82 Å. X-rays incident on the surface of the crystal is found to give rise to first order Bragg reflection at glancing angle 8.8°. Calculate the wavelength of X-rays.

Soln. According to Bragg's law $2d\sin\theta = n\lambda$.

Here, $d = 2.82\text{Å} = 2.82\times10^{-10}\text{ m}, \theta = 8.8°$

$\Rightarrow$ $\sin\theta = 0.153, n = 1$

$\Rightarrow$ $2\times2.82\times10^{-10}\times0.153 = \lambda$

$\Rightarrow$ $\lambda = 0.863\times10^{-10}\text{ m} = 0.863\text{Å}$

Example: Calculate the glancing angle on the plane (110) of a cubic rock salt crystal (a = 2.81Å) corresponding to second order diffraction maxima of wavelength 0.71Å

Soln. Spacing for (110) plane, $d = \dfrac{a}{\sqrt{1^2+1^2+0}} = \dfrac{a}{\sqrt{2}}\text{Å} = \dfrac{2.81}{\sqrt{2}} = 1.993\text{Å}$

Now, $2d\sin\theta = n\lambda;\ \lambda = 0.71\times10^{-10}\text{m};\ n = 2$

$\Rightarrow$ $\sin\theta = \dfrac{n\lambda}{2d} = \dfrac{2\times0.71\times10^{-10}}{2\times1.993\times10^{-10}} = 0.3562 \Rightarrow \theta = 20.87\text{Å}$

Example: The molecular weight of rock salt (a simple cubic) crystal is 58.5 kg per kilo-mole and its density is $2.16\times10^3\text{ kg/m}^3$. Taking Avogadro's number = 6.02×10^{26}, calculate the grating space d_{100} of rock salt.

Using this value of lattice constant, calculate the lattice constant, calculate the wavelength of X-rays in second order, if angle of diffraction $\theta = 26°$.

Soln. Mass of one kilo-mole of NaCl = 58.5 kg.

Number of molecules in one kilo-mole = 6.02×10^{26}

Therefore, mass of NaCl crystal = $2.16\times10^3\text{ kg/m}^3$.

Volume of one NaCl molecule $= \dfrac{9.72\times10^{-26}}{2.16\times10^3} = 4.5\times10^{-29}\text{ m}^3$

As there are two atoms per NaCl molecule, the volume per atom $= \dfrac{4.5\times10^{-29}}{2} = 2.25\times10^{-29}\text{ m}^3$

If 'd' is the atomic spacing for NaCl crystal, then volume per atom = d^3.

$\Rightarrow$ $d^3 = 2.25\times10^{-29}$

$\Rightarrow$ $d = \left[2.25\times10^{-29}\right]^{1/3} = 2.82\times10^{-10}\text{m} = 2.82\text{ Å}$

$\Rightarrow \quad d_{100} = 2.82\text{Å}$

According to Bragg's law $2d\sin\theta = n\lambda$

Here, $d = 2.82\times10^{-10}\text{ m}, \theta = 26^\circ \quad \Rightarrow \sin\theta = 0.4383$

and $n = 2$

$\Rightarrow \quad 2\lambda = 2\times2.82\times10^{-10}\times0.4383$

$\Rightarrow \quad \lambda = 2.82\times0.4383\times10^{-10} = 1.24\times10^{-10}\text{m} = 1.24\text{Å}$

Example: (a) If X-rays of wavelength 0.5Å are diffracted at an angle of 5° in the first order, what is the spacing between the adjacent planes of the crystal? At what angle will second maximum occur?
(b) The Bragg angle for the first order reflection from (111) plane in a crystal is 60°. Calculate the interatomic spacing if X-rays of wavelength 1.8×10^{-10} m are used.

Soln. (a) According to Bragg's law $2d\sin = n\lambda$

Here, $\lambda = 0.5\text{Å} = 0.5\times10^{-10}\text{m}; \theta = 5^\circ$

$\Rightarrow \quad \sin\theta = 0.0871; n = 1$

$\Rightarrow \quad 2d\times0.871 = 0.5\times10^{-10}$

$\Rightarrow \quad d = \dfrac{0.5\times10^{-10}}{0.1742} = 2.87\times10^{-10}\text{m} = 2.87\text{Å}$

For second order maximum, let θ' be the angle of Bragg reflection, then

$2d\sin\theta' = 2\lambda$

$\Rightarrow \quad \sin\theta' = \dfrac{\lambda}{d} = \dfrac{0.5\times10^{-10}}{2.87\times10^{-10}} = 0.1742$

$\Rightarrow \quad \theta' = 10.03^\circ$

(b) According to Bragg's law, $2d\sin\theta = n\lambda$.

Here, $\theta = 60^\circ \quad \Rightarrow \sin\theta = \sin60 = 0.866, \lambda = 1.8\times10^{-10}\text{ m}; n = 1$

$\Rightarrow \quad 2d\times0.866 = 1.8\times10^{-10}$

$\Rightarrow \quad d = \dfrac{1.8\times10^{-10}}{1.732} = 1.039\times10^{-10}\text{ m}$

This gives us d_{111} $\quad d_{111} = 1.039\times10^{-10}\text{ m}$

If the interatomic spacing for a simple cubic lattice.

$\Rightarrow \quad d_{100} = a$, then $d_{111} = \dfrac{a}{\sqrt{3}}$

$\Rightarrow \quad a = d_{100} = d_{111}\times\sqrt{3} = 1.039\times1.732\times10^{-10}\text{m} = 1.8\times10^{-10}\text{ m}$

Example: From the following data calculate the wavelength of neutron beam and its speed. Spacing between successive (100) planes = 3.84Å; grazing angle 30°; order of Bragg reflection = 1.

Soln. According to Bragg's relation, $2d\sin\theta = n\lambda$

Here, $d = 3.84\text{Å} = 3.84\times10^{-10}\text{ m}, \quad \theta = 30^\circ; \sin30 = \dfrac{1}{2}; n = 1$

$\Rightarrow \quad 2\times3.84\times10^{-10}\times\dfrac{1}{2} = 1\times\lambda$

$\Rightarrow \quad \lambda = 3.84\times10^{-10}\ m = 3.84Å$

According to de-Broglie relation, $\lambda = \frac{h}{p} = \frac{h}{mv}$

where 'h' is Planck's constant having a value 6.62×10^{-34} Js and neutron mass 'm' $= 1.67\times10^{-27}$ kg

$$\Rightarrow \quad v = \frac{h}{m\lambda} = \frac{6.62\times10^{-34}}{1.67\times10^{-27}\times3.84\times10^{-10}} = 1.03\times10^{3}\ ms^{-1}$$

• Ewalid's construction:

Ewald's construction is a geometrical construction to get a relation between wave vector $\vec{k}$ and the direction of incident X-ray beam with the help of reciprocal lattice and thus derive Bragg's law in vector form.

Draw a vector $\vec{OA} = \vec{k} = \frac{2\pi}{\lambda}$ in the direction of incident X-ray beam originating at O and terminating at any reciprocal lattice point A. Draw a sphere of radius $k = \frac{2\pi}{\lambda}$ with origin O as centre. This sphere is konwn as reflex sphere (The section of this sphere in a plane is a circle). Suppose this sphere intersects some point B of the reciprocal lattice whose indices are $(h'k'\ell')$, then $\vec{AB}$ represents the reciprocal lattice vector $\vec{G}$ and is normal to some set of direct lattice planes e.g., ON. $AB = |\vec{G}| = \frac{2\pi n}{d}$

where 'n' is the largest integral factor common to numbers $(h'k'\ell')$ and 'd' is the iner-planer spacing for the set.

• Bragg's diffraction condition in terms of reciprocal lattice:

As the wave vector $\vec{OA} = \vec{k}$ is the incident wave vector, $\vec{OB} = \vec{k}'$ is the diffracted (or reflected) wave vector and is given by

$$\vec{k}' = \vec{k} + \vec{G}$$

This shows that scattering changes only the direction of the wave vector $\vec{k}$ and the scattered wave vectors differes from the incident wave vector by a reciprocal lattice vector $\vec{G}$.

For the diffraction, the magnitude of $(\vec{k}+\vec{G})$ must be equal to the wave vector $\vec{k}'$.

i.e. $$\vec{k}'^2 = (\vec{k}+\vec{G})^2 = (\vec{k}+\vec{G}).(\vec{k}+\vec{G}) = k^2 + 2\vec{k}.\vec{G} + \vec{G}.\vec{G}$$

But the magnitude of $\vec{k}'$ = magnitude of $\vec{k}$

$\Rightarrow \quad \vec{k}'^2 = k^2$

Hence relation (i), becomes,

$$2\vec{k}.\vec{G} + \vec{G}.\vec{G} = 0 \qquad \Rightarrow 2\vec{k}.\vec{G} + G^2 = 0$$

$$\Rightarrow \quad \left(\vec{k} + \frac{\vec{G}}{2}\right).\vec{G} = 0$$

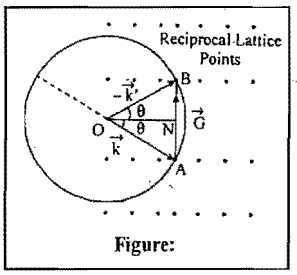


Figure:

This is Bragg's law in vector form and gives the Bragg's diffraction conditions in terms of reciprocal lattice vector $\vec{G}$.

Example: The X-ray powder photograph of a cubic substance taken with Cu K_α radiation $\lambda = 1.54$ Å. Shows diffraction lines at Bragg angle 12.3°, 14.2°, 20.4° and 24.1°. Determine the miller indices of all the lines and size of the cubic and unit cell.

Soln. $\because \quad 2d\sin\theta = n\lambda \qquad (n=1)$

$$d_{nk\ell} = \frac{a}{\sqrt{h^2+k^2+\ell^2}}, \qquad \frac{2a}{\sqrt{h^2+k^2+\ell^2}}\sin\theta = \lambda$$

$$\Rightarrow \frac{4a^2\sin^2\theta}{h^2+k^2+\ell^2} = \lambda^2 \qquad h^2+k^2+\ell^2 = \frac{4a^2}{\lambda^2}\sin^2\theta \qquad \Rightarrow \sin^2\theta = \frac{\lambda^2}{4a^2}\left(h^2+k^2+\ell^2\right)$$

$$\sin(12.3) = \frac{1.54}{2a}\sqrt{3} \qquad \sin\theta_1 = \frac{\lambda}{2a}\sqrt{h_1^2+k_1^2+\ell_1^2} \qquad a = 6.26 \text{ Å}.$$

$$\left(h_1^2+k_1^2+\ell_1^2\right):\left(h_2^2+k_2^2+\ell_2^2\right):\left(h_3^2+k_3^2+\ell_3^2\right):\left(h_4^2+\ell_4^2+k_4^2\right)$$

$$= \sin^2\theta_1 : \sin^2\theta_2 : \sin^2\theta_3 : \sin^2\theta_4$$

$$= 0.04538 : 0.060 : 0.125 : 0.1667$$

$$= 1 : \frac{0.060}{0.04538} : \frac{0.125}{0.04538} : \frac{0.1667}{0.04538}$$

$$= 1 : 1.33 : 2.67 : 3.67$$

$$= 1 : 4/3 : 8/3 : 11/3$$

$$= 3 : 4 : 8 : 11$$

$$= (111) \quad (200) \quad (220) \quad (311)$$

$\therefore$ system is fcc

Example: The powder diffraction pattern of a bcc crystal is recorded by using Cu K_α radiation of X-rays of wave length 1.54 Å

(i) If the (0 0 2) planes diffrated at 60° then lattice parameter a is:

(a) 2.67Å **(b)** 3.08Å **(c)** 3.56Å **(d)** 5.34 Å

(ii) Assuming the atomic mass of constituents atoms to be 50.94 amu the density of the crystal in units of kg/m^3 is:

(a) 3.75×10^3 **(b)** 4.45×10^3 **(c)** 5.79×10^3 **(d)** 8.89×10^3

Soln. (i) $\lambda = 1.54$Å, $d = \frac{a}{2}$

Angle of diffraction is $2\theta = 60°$.

$\boxed{\theta = 30°}$

$2d\sin\theta = n\lambda, \qquad \boxed{n=1}$

$\Rightarrow \quad \boxed{d_{hk\ell} = \frac{a}{2}} \quad \Rightarrow \quad 2\times\frac{a}{2}\sin\theta = \lambda \quad \Rightarrow \quad a\times\frac{1}{2} = 1.54$

$a = 3.08$ Å

(ii) $m_A = 50.94$ amu

$\frac{n}{a^3} = \frac{N_A \rho}{M_A}$ $N_A \rightarrow$ Avagadro number

$\rho \rightarrow$ Mass density

$\boxed{n = 2}$ $n \rightarrow$ Number of atom/unit cell

$$\frac{2}{(3.08)^3} = \frac{M_A \rho}{50.94}$$

Ans. $\rho = \frac{50.94 \times 2}{(3.08)^3 \times 1.6 \times 10^{26}} = 5.79 \times 10^3$

Example: A metal with bcc structure shows the first (smallest angle) diffraction peak at a Bragg angle of $\theta = 30°$. The wave length of X-ray used is 2.1 Å. The volume of the primivitve unit cell of the metal is:

(a) 26.2(Å)^3 (b) 13.1 Å^3 (c) 9.3 Å^3 (d) 4.6 Å^3.

Soln. $2d_{nkl} \sin\theta = \lambda$ first peak per bcc is (110)

$$2d_{nkl}\frac{1}{2} = \lambda, \quad \frac{2}{2}d_{110} = \lambda \quad \Rightarrow \frac{2}{2}.\frac{a}{\sqrt{2}} = \lambda$$

$\boxed{a = (2.1)\sqrt{2}\text{Å}}$

Volume of primitive unit cell $= \frac{(2.1)^3 \times (\sqrt{2})^3}{2} = \frac{a^3}{2} = 13.1\ \text{Å}^3$

$\frac{n}{a^3} = \frac{N_A \rho}{M_A}$ $N_A \rightarrow$ Avagadro number

$\rho \rightarrow$ Mass density

$\boxed{n = 2}$ $n \rightarrow$ Number of atom/unit cell

$$\frac{2}{(3.08)^3} = \frac{M_A \rho}{50.94}$$

Ans. $\rho = \frac{50.94 \times 2}{(3.08)^3 \times 1.6 \times 10^{26}} = 5.79 \times 10^3$

Example: The angle of reflection of neutron beam from a crystal of inter planer spacing is 30°, the speed of neutrons will be

(a) 1.03×10^6 cm/s (b) 1.03×10^5 cm/s (c) 1.03×10^4 cm/s (d) 1.03×10^4 cm/sec

Soln. Since, $2d\sin\theta = \lambda \Rightarrow 2 \times 3.84 \sin 30° = \lambda \Rightarrow \lambda = 3.84\text{Å} = 3.84 \times 10^{-8}$cm

Since, $\lambda = \frac{h}{p} = \frac{h}{mv} \Rightarrow v = \frac{h}{m\lambda} = \frac{6.6 \times 10^{-34}}{1.67 \times 10^{-27} \times 2.84 \times 10^{-8}}$

$= 1.03 \times 10^5$ cm/s

Example: Zinc crystallises in hcp structure, If r is the radius of zinc atom, the height of the unit cell is

(a) $2r\left(\frac{8}{3}\right)^{1/2}$ (b) $r\left(\frac{8}{3}\right)^{1/2}$ (c) $2r\left(\frac{3}{8}\right)^{1/2}$ (d) $r\left(\frac{3}{8}\right)^{1/2}$

Soln. Since, for hcp $\frac{c}{a}=\sqrt{\frac{8}{3}} \Rightarrow c=\sqrt{\frac{8}{3}}a \Rightarrow c=\sqrt{\frac{8}{3}}.2r =$ height of the unit cell

(for hcp, $2r = a$)

Example: A two dimensional lattice has the basic vectors $\vec{a} = 2\hat{i}$, $\vec{b} = \hat{i} + 2\hat{j}$. The basic vectors of the reciprocal lattice will be

(a) $\frac{1}{2}\left(\hat{i}-\frac{1}{2}\hat{j}\right), \frac{\hat{j}}{2}$ (b) $\frac{1}{4}\left(\hat{i}-2\hat{j}\right), \frac{\hat{j}}{4}$ (c) $2\left(\hat{i}-\frac{\hat{j}}{2}\right), 2\hat{j}$ (d) $4\left(\hat{i}-\frac{\hat{j}}{2}\right), 4\hat{j}$

Soln. Let a vector $\vec{c} = \hat{k}$

Since, $\vec{a}' = \frac{\vec{b}\times\vec{c}}{a.(\vec{b}\times\vec{c})}$ $\vec{b}' = \frac{\vec{c}\times\vec{a}}{\vec{a}.(\vec{b}\times\vec{c})}$

Therefore, $\vec{a}' = \frac{1}{4}(2\hat{i}-\hat{j})$ and $\vec{b}' = \frac{1}{4}\times 2\hat{j} = \frac{\hat{j}}{2}$

Problem: An electron beam of 4keV is diffracted through Bragg's angle of 16° for the first maxima. If energy is increased to 16 K eV the corresponding Bragg's angle of diffraction will be nearly

(a) 4° (b) 8° (c) 12° (d) 16°

• Crystal Bonding:

The ability to hold the atoms or ions together is called bonding.

Types of bonding:

The individual atoms of a crystalline solid are held together as one system with different types of bonds existing between them. These bonds are classified into five idealised types.

(i) Ionic bonding. Examples: NaCl, LiF (Due to transfer to valence electrons)

(ii) Co-valent bonding. Examples: diamond, SiC(Sharing of valence electrons)

(iii) Van der waal bonding. Example: solid Argon (electrons remain associated with original molecules).

(iv) Hydrogen bonding. Example: ice.

(v) Metallic bonding. Cu, Ag, Fe are examples. (valence electrons are essentially free)

• Cohesion energy:

From the very existence of solids, two general conclusions can be drawn.

(i) There must be an attractive force between atoms or molecules in a solid which keeps them together

(ii) There must also be a repulsive force acting between the atoms. This is why large external pressure is required to compress a solid to any appreciable extent.

When two identical or non-identical atoms, which form a molecule, are brought from infinity to a close proximity, they first attract each other and other and then, if they are brought closer than a certain distance, repel each other. In other words, a kind of spring effect takes place. As the potential V is related to the force by the relation $F = \frac{-dV}{dr}$, the resulting potential is a function of distance of separation 'r'. The variation of corresponding potential energy V in eV with distance 'r' in Å is shown in figure.

The attractive force gives rise to a negative potential and the repulsive force gives rise to a positive potential shown by dotted curves. The resultant potential enegy is shown by full line curve. It has a minimum at a distance r_0 and represents the equilibrium position, where the attractive and the repulsive forces balance each other and potential energy has a maximum negative value. The potential energy $V(r_0)$ at a distance r_0 is thus responsible for keeping the atoms bound in a solid and gives the cohesive or bonding energy of the solid.

The potential energy $V(r_0)$ is a negative quantity. The positive quantity $-V(r_0) = D$ is called the dissociation energy of the molecule.

The cohesive energy of a solid is defined as the energy which will be given out in the process of the formation of a crystal by bringing neutral atoms from infinity to the position of equilibrium separation.

If the potential energy due to attraction V_a is supposed to vary as the m^{th} power of the distance and that due to repulsion V_r as n^{th} power of r, then

$$V_a \propto \frac{1}{r^m} = -\frac{A}{r^m} \text{ and } V_r \propto \frac{1}{r^n} = \frac{B}{r^n}$$

Therefore, resultant potential or cohesive energy,

$$V = V_a + V_r = -\frac{A}{r^m} + \frac{B}{r^n}$$

where 'A' and 'B' are constants of proportionality. The cohesive enegy is generally expressed in eV per atom.

The force between the two atoms is given by

$$F = \frac{-dV}{dr} = \frac{mA}{r^{m+1}} - \frac{nB}{r^{n+1}}$$

At $r = r_0$ the attractive and repulsive forces balance each other and $F(r_0) = 0$. In other words at $r = r_0$.

$$\frac{mA}{r_0^{m+1}} - \frac{nB}{r_0^{n+1}} = 0 \qquad \Rightarrow \frac{m}{n} = \frac{B}{A} r_0^{m-n}$$

$$\Rightarrow \qquad r_0^{m-n} = \frac{A}{B}\frac{m}{n} \qquad \ldots(i)$$

Hence, the potential energy in the equilibrium state,

$$V(r_0) = \frac{-A}{r_0^m} + \frac{B}{r_0^n} = \frac{-A}{r_0^m}\left[1 - \frac{B}{A} r_0^{m-n}\right] = \frac{-A}{r_0^m}\left[1 - \frac{m}{n}\right]$$

Although the attractive and repulsive forces are in equilibrium at $r = r_0$, the potential energy is not zero as $m \neq n$. If $n >> m$ the total energy is essentially the energy of attraction given by $-\frac{A}{r_0^m}$.

For the potential energy to have a minimum at $r = r_0$ we have $\left|\frac{d^2V}{dr^2}\right|_{r=r_0} > 0$, i.e. it must be positive.

Now, $$\frac{d^2V}{dr^2} = \frac{-m(m+1)A}{r^{m+2}} + \frac{n(n+1)B}{r^{n+2}} > 0$$

Substituting the value of $r = r_0$ from (i), we have

$$-m(m+1)A \times \frac{B}{A}\frac{n}{m}\left(\frac{1}{r_0^{n+2}}\right) + \frac{n(n+1)B}{r_0^{n+2}} > 0$$

$\Rightarrow \quad -m-1+n+1>0$

$\Rightarrow \quad n-m>0 \qquad \Rightarrow n>m$

In other words, a minimum in the energy curve is possible only if $n > m$. Thus the formation of a chemical bond requires that the repulsive forces be of shorter range than the attractive forces.

The energy $V(r_0)$ at the equilibrium distance r_0 is called the binding energy, the energy of cohesion or dissociation energy of the molecule. This much energy is required to separate the atoms of a diatomic molecule to an infinite distance apart.

The cohesive energy may also be defined as the energy released when two atoms are brought close to each other at the equilibrium distance r_0.

Larger the energy released, more stable the bond formed and hence more stable is the crystal structure.

• Expression for the cohesive energy of ionic crystals:

The coulomb energy of attraction between two ions seperated by a distance r is

$$U_{attraction} = -\frac{e^2}{4\pi \epsilon_0 r} \qquad \ldots (1)$$

In the crystal, each ion interacts with all its neighbouring ions of the same as well as of opposite signs. To take this into account, the net energy of attraction per ion-pair may be written as

$$U_{att} = \frac{-\alpha e^2}{4\pi \epsilon_0 r} \qquad \ldots (2)$$

Where α is the correction factor, called 'Madelung constant'. For simple crystals α-lies between 1.6 and 1.8 for NaCl $\alpha = 1.748$ and 1.763 for CsCl.

Now, in an ionic crystal as two ions approach each other under coulomb attraction, at a certain distance apart, they begin to repel each other with a force which rise very rapidly with decreae in distance.

$$\therefore \quad U_{rep} = \frac{B}{r^n} \qquad \ldots (3)$$

$$\therefore \quad \text{The total P.E. } (U) = U_{att} + U_{rep} = -\alpha \frac{e^2}{4\pi \epsilon_0 r} + \frac{B}{r^n} \qquad \ldots (4)$$

At equilibrium distance $r = r_0$, U = minimum.

$$\therefore \quad \left.\frac{dU}{dr}\right|_{r=r_0} = 0 = \frac{\alpha^2 e^2}{4\pi \epsilon_0 r_0^2} - \frac{nB}{r_0^{n+1}}$$

$$\Rightarrow \quad B = \frac{\alpha e^2}{4\pi \epsilon_0 n} r_0^{n-1}$$

$$\therefore \quad \boxed{U|_{r=r_0} = -\frac{\alpha e^2}{4\pi \epsilon_0 r_0} + \frac{\alpha e^2}{4\pi \epsilon_0 r_0 n} = \frac{-\alpha e^2}{4\pi \epsilon_0 r_0}\left(1-\frac{1}{n}\right)} \qquad \ldots (5)$$

SUMMARY

1. There are two types of forces exsiting amongst the atoms of a crystal: the long range Coulombic forces which are attractive in nature and the short range repulsive forces.

2. The total potential energy of a system of atoms is expressed as

$$U = -A/r^m + B/r^n$$

where r ist he interatomic distance and A, B, m and n are constants. Generally, n>m. The first term represents the energy of attraction and the second one represents the energy of repulsion.

3. A stable chemical bond is formed at an equilibrium interatomic distance r_0 where the forces of attraction balance the forces of repulsion and the total energy U becomes the minimum. The minimum enregy is called the binding energy, bond energy, energy of cohesion or dissociation energy of a molecule and is giveb by

$$U_0 = \left(-A/r_0^m\right)(1-m/n)$$

4. An ionic bond between two atoms is formed by the transfer of eleetrons from one atom to the other. It is non-directional.

5. A covalent or valence bond results from the localized sharing of an equal number of valence electrons of the neighbouring atoms. It is a directional bond.

6. In metallic bond, the sharing of electrons is partial and delocalized. A metal may be considered as an array of positive ions which are held together in a free-electron cloud. Hence the metallic bond is non-directional.

7. The van der waals forces or dispersion bodns result from the dipole induced dipole interactions amongst the neighbouring inert gas atoms or the molecules of some other gases. These are non-directional. The crystals having these types of forces are called molecular crystals.

8. Hydrogen bond is a an electrostatic attraction between the neighbouring molecular dipoles each containing a hydrogen atom. In case the molecules do not contain hdyrogen atoms, the bond is termed dipole bond. These are directional bonds.

9. The lattice energy or the total binding energy of an ionic crystal is given by

$$U_{total} = NU_i = -\left(N\alpha q^2/R_0\right)\left[1-\rho/R_0\right]$$

where U_i is the cohesive energy of the i^{th} ion, N is the number of ionic molecules, r_0 is the nearest neighbour equilibrium distance, q is the electronic charge, ρ is the range of repulsive interaction and α is the Madelung constant. The term within the parentheses represents the Madelung energy

10. The range ρ can be determined from the bulk modulus B of ionic crystal. For NaCl, the two are related as

$$B = \frac{\alpha q^2}{18R_0^4}\left(R_0/\rho - 2\right)$$

Example: The energy of two particles in the field of each other at a separation 'r' is given by $U = \frac{\alpha}{r} + \frac{\beta}{r^8}$. where α and β are constants. At what separation they will form a stable compound?

Soln. The energy of two particles in the field of each other at a separation 'r' is given by $U = \frac{\alpha}{r} + \frac{\beta}{r^8}$

They will form a stable compound at a separation r_0 such that at that separation the energy U is a minimum, i.e.

$$\left|\frac{dU}{dr}\right|_{r=r_0} = 0 \quad \Rightarrow \quad \frac{dU}{dr} = -\frac{\alpha}{r^2} - \frac{8\beta}{r^9}$$

$$\Rightarrow \quad \left|\frac{dU}{dr}\right|_{r=r_0} = -\frac{\alpha}{r_0^2} - \frac{8\beta}{r_0^9} = 0$$

$$\Rightarrow \quad \frac{\alpha}{r_0^2} + \frac{8\beta}{r_0^9} = 0 \quad \Rightarrow \alpha = \frac{8\beta}{r_0^7}$$

$$\Rightarrow \quad r_0^7 = \frac{8\beta}{\alpha}. \text{ Hence } r_0 = \left[\frac{8\beta}{\alpha}\right]^{1/7}$$

Example: The energy of two particles in the field of each other is given by $U = -\frac{\alpha}{r^2} + \frac{\beta}{r^{10}}$ where α and β are constants and r, the separation between the particles. Determine the separation between the particles for a stable compound and also determine the cohesive energy of crystal.

Soln. The energy of the two particles in the field of each other at a separation 'r' is given by

$$U = -\frac{\alpha}{r^2} + \frac{\beta}{r^{10}} \qquad \ldots (i)$$

They will form a stable compound at a separation r_0 such that at that separation the energy U is minimum i.e.,

$$\left|\frac{dU}{dr}\right|_{r=r_0} = 0$$

$$\Rightarrow \quad \frac{dU}{dr} = \frac{2\alpha}{r^3} - \frac{10}{r^{11}} = 0 \quad \Rightarrow \quad r^8 = \frac{5\beta}{\alpha}$$

Therefore, separation for a stable compound $r_0 = \left[\frac{5\beta}{\alpha}\right]^{1/8}$

Putting the value of $r = r_0$ in equation (i), we have

$$U_{min} = -\alpha\left(\frac{\alpha}{5\beta}\right)^{1/4} + \beta\left(\frac{\alpha}{5\beta}\right)^{5/4} = \frac{\alpha^{5/4}}{(5\beta)^{1/4}}\left[\frac{\beta}{5\beta} - 1\right] = -\frac{4}{5}\left[\frac{\alpha^{5/4}}{(5\beta)^{1/4}}\right]$$

$$= -\frac{4\alpha}{5}\left[\frac{\alpha}{5\beta}\right]^{1/4} = -\frac{4\alpha}{5r_0^2} = -\frac{4}{5}\left(\frac{\alpha}{r_0^2}\right)$$

Therefore, Cohesive energy of the crystal $U_{min} = -\frac{4}{5}\left(\frac{\alpha}{r_0^2}\right)$

Chapter-3: BAND THEORY OF SOLIDS

• Periodic Potential in a Crystalline Solid:

Consider an electron in the vicinity of an atomic nucleus of charge Ze. The potential energy of the electron in SI units is given by

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r} \qquad \ldots(1)$$

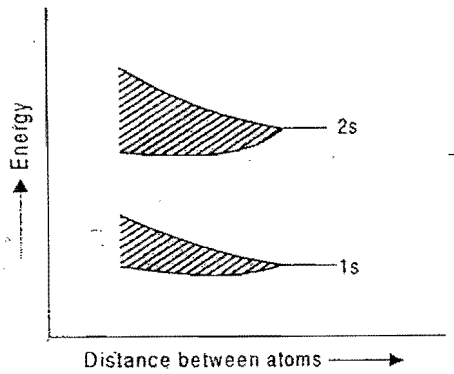


Figure: Formation of bands for 1s and 2s states.

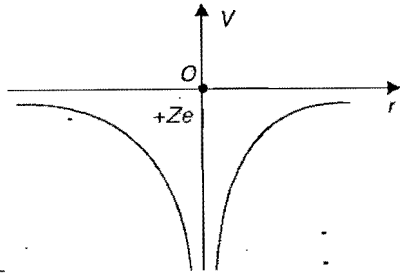


Figure: Variation of potential energy with distance for an isolated atom.

where ε_0 is the free-space permitivity and 'r' is the distance of the electron from the nucleus. The variation of the potential energy with the distance 'r' is shown in figure. When a number of such atomic nuclei are brought close together to form a crytal, the potential energy of an electron is obtained by summing up the potential energies due to the individual nuclei. Thus the potential energy as a function of distance for an infinite one-dimensional crystal would be as shown in figure. Note that the potential energy is a periodic function of distance, the atomic nuclei being equipspaced.

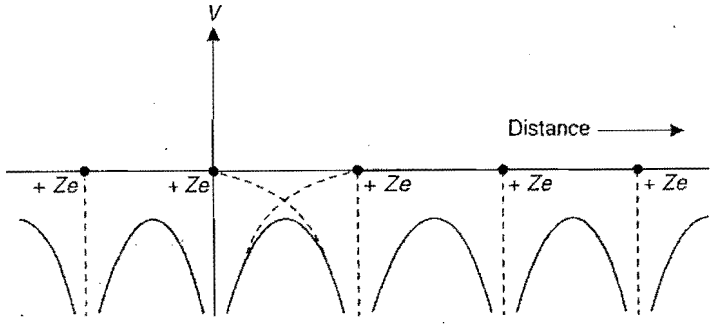


Figure: Variation of potential energy with distance for a one-dimensional crystal.

• The Kroning-Penney Model:

In this model, for the sake of convenience, the periodic potential energy curve of figure is approximately by square well,s as shown in figure . Let the period of hte periodic potential be (a + b).

For, $-b < x < 0$, the potential energy is V_0 while for $0 < x < a$, the potential energy is zero. The Schrodinger equations are

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}E\psi = 0 \qquad \text{for } 0 < x < a \qquad \ldots(2)$$

$$\Rightarrow \quad \frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0 \qquad \text{for } -b < x < 0 \qquad \ldots(3)$$

We assume that the electron energy E is less than V_0. Let

$$\alpha^2 = \frac{2mE}{\hbar^2} \qquad \Rightarrow \beta^2 = \frac{2m}{\hbar^2}(V_0 - E) \qquad \ldots(4)$$

Then equation (2) and (3) become

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0 \qquad \text{for } 0 < x < a \qquad \ldots(5)$$

$$\Rightarrow \quad \frac{d^2\psi}{dx^2} - \beta^2\psi = 0 \qquad \text{for } -b < x < 0 \qquad \ldots(6)$$

The potential is periodic, i.e.,

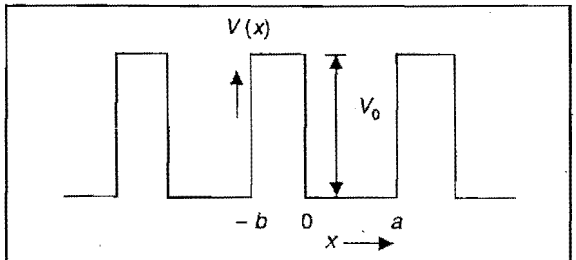


Figure: The Kroning-Penney model potential

$$V(x) = V(x + a + b) \qquad \ldots(7)$$

Bloch's theorem state that for a periodic potential of the form of equation (7), the solution of the Schrodinger equations are of the form

$$\psi = u_k(x)\exp(ikx) \qquad \ldots(8)$$

where $u_k(x)$ is a periodic function with the peridicity of lattice, i.e.,

$$u_k(x) = u_k(x + a + b) \qquad \ldots(9)$$

Wave functions of the form of equation (9) are called Bloch functions. Substituting equation (8) into equation (2) and (3), we obtain

$$\frac{d^2u}{dx^2} + 2ik\frac{du}{dx} + (\alpha^2 - k^2)u = 0, \qquad 0 < x < a \qquad \ldots(10)$$

$$\Rightarrow \qquad \frac{d^2u}{dx^2}+2ik\frac{du}{dx}-\left(\beta^2+k^2\right)u=0, \qquad -b<x<0 \qquad \ldots(11)$$

The solutions of equation (10) and (11) are

$$u_1=A\exp\left[i(\alpha-k)x\right]+B\exp\left[-i(\alpha+k)x\right], \qquad 0<x<a \qquad \ldots(12)$$

$$u_2=C\exp\left[\beta-ik)x\right]+D\exp\left[-(\beta+ik)x\right], \qquad -b<x<0 \qquad \ldots(13)$$

where A, B, C and D are constants. These constants are determined in such a way that the wave function ψ and its normal derivative $d\psi/dx$ are single-valued and continuous. That is,

$$u_1(0)=u_2(0),\ u_1(a)=u_2(-b),$$

$$\left(\frac{du_1}{dx}\right)_{x=0}=\left(\frac{du_2}{dx}\right)_{x=0} \Rightarrow \left(\frac{du_1}{dx}\right)_{x=a}=\left(\frac{du_2}{dx}\right)_{x=-b} \qquad \ldots(14)$$

Using these conditions equations ( ) and ( ), we get

$$A+B=C+D \qquad \ldots(15)$$

$$i(\alpha-k)A-i(\alpha+k)B=(\beta-ik)C-(\beta+ik)D \qquad \ldots(16)$$

$$A\exp\left[i(\alpha-k)a\right]+B\exp\left[-i(\alpha+k)a\right]=C\exp\left[-(\beta-ik)b\right]+D\exp\left[(\beta+ik)b\right] \qquad \ldots(17)$$

$$\Rightarrow \qquad i(\alpha-k)A\exp\left[i(\alpha-k)a\right]-i(\alpha+k)B\exp\left[(\beta+ik)b\right] \qquad \ldots(18)$$

Equations (15) through (18) are homogeneous and will have a solution other than $A=B=C=D=0$, provided the determinant of the coefficients A, B, C and D vanishes. Expanding this determinant and simplifying, we obtain.

$$\frac{\beta^2-\alpha^2}{2\alpha\beta}\sin\beta b\sin\alpha a+\cosh\beta b\cos\alpha a=\cos k(a+b) \ldots(19)$$

From $E>V_0$, β imaginary. For such energies we put $\beta=i\gamma$ and note that $\sinh i\gamma b=i\sin\gamma b$ and $\cosh i\gamma b=\cos\gamma b$. Then we obtain from equation (19)

$$-\frac{\alpha^2+\gamma^2}{2\alpha\gamma}\sin\gamma b\sin\alpha a+\cos\gamma b\cos\alpha a=\cos k(a+b) \qquad \ldots(20)$$

It is convenient to use equation (19) when $0<E<V_0$ and equation (20) when $E>V_0$. Equations (19) and (20) may also be written respectively in the forms.

$$\left[1+\frac{\left(\beta^2+\alpha^2\right)^2}{4\alpha^2\beta^2}\sin^2\beta b\right]^{1/2}\cos(\alpha a-\theta)=\cos k(a+b) \ldots(21)$$

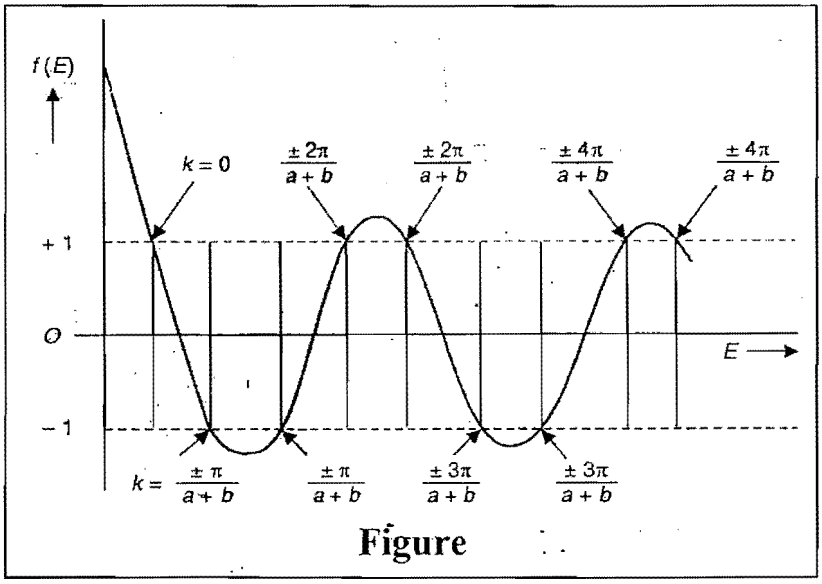
where, $$\tan\theta=\frac{\beta^2-\alpha^2}{2\alpha\beta}\tanh\beta b,$$

$$\Rightarrow \qquad \left[1+\frac{\left(\alpha^2-\gamma^2\right)^2}{4\alpha^2\gamma^2}\sin^2\gamma b\right]\cos(\alpha a-\theta)=\cos l(a+b) \qquad \ldots(23)$$

where $$\tan\theta=-\frac{\alpha^2+\gamma^2}{2\alpha\gamma}\tan\gamma b$$

In equation (19) and (20) the left-hand sides are cosine functions multiplied by factors which are greater than unity. The multiplying factor is a maximum for $\alpha = 0$, i.e. for $E = 0$, and approaches unity for large energies when $\alpha^2 = -\beta^2$.

Equations (19) and (20) are transcendental in nature and may be solved graphically. The left-hand side of either of these equations is plotted as a function of E in figure below. The right-hand side of each equation is $\cos k(a+b)$ which lies between +1 and −1. Thus physically acceptable solutions are possible when the left-hand side of equation (19) or (20) lies between +1 and −1. The corresponding energy values are permitted. Outside these limits, physical solutions are not possible and the corresponding energies are forbidden. Thus, allowed and forbidden energy bands are alternately produced. The forbidden energy bands are shown as shaded regions in figure below.



Figure

With the help of figure above, i.e. equation (19) and (20), one can plot the energy E as a function of the wave vector k. Such a plot is shown in figure. The edges of the allowed bands occur when $\cos k(a+b) = \pm 1$, i.e. when $k = \pm \frac{n\pi}{a+b}$, where 'n' is zero or an integer. The E–k diagram has the following important features:

(i) As $E \to \infty$, the E-k relationship approaches that for a free electron; i.e. we have $E = \hbar^2 k^2 / 2m_0$ which is shown as a dotted curve in figure.

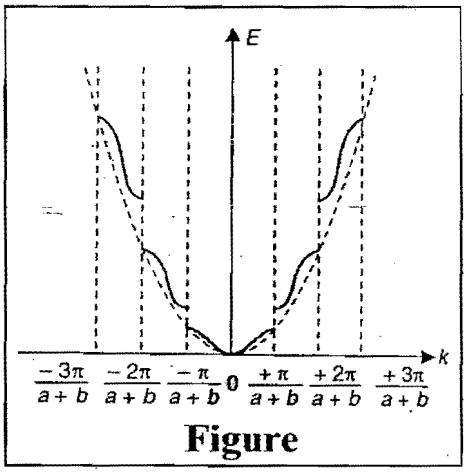
(ii) For large energies, the allowed bands are broad and the forbidden bands are narrow.

(iii) If the wells are deep and widely spaced, i.e. if b and V_0 are large, a low energy electron will be practically bound to one of the wells. Thus the low energy eigenvalues will be nearly equal to those of a single well. If the wells are close together, the levels spread into energy bands. As the separation 'b' is reduced, the allowed bands become wider.

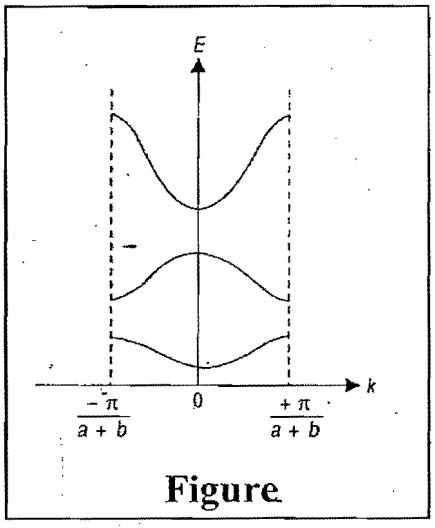
(iv) As the barrier height V_0 is increased with 'a' and 'b' remaining fixed, the widths of the energy bands decrease.

(v) At the edges of the allowed bands, i.e. at $k = \pm \frac{n\pi}{a+b}$, the slope of the E-k curve is zero.

Reduced Zone representation:



Figure



Figure

In figure above the region extending from $k = -\frac{\pi}{a+b}$ to $k = \frac{\pi}{a+b}$ is called the first Brillouin zone, that from $-2\pi/(a+b)$ to $-\pi/(a+b)$ and from $\pi/(a+b)$ to $2\pi/(a+b)$ is known as the second Brillouin zene, and so on. In equation (19) and (20) if 'k' is replaced by $k+\left[2n\pi/(a+b)\right]$ where 'n' is an integer, positive or negative, the equations are still satisfied since such replacements do not alter the value of $\cos k(a+b)$. Thus 'k' is not uniquely determined, and it is often very userful to translate the various segments of the E-k curve in figure parallel to the k-axis through distances that are integral multiples of $2\pi/(a+b)$ so that k lies within the region $-\pi/(a+b) \le k \le \pi/(a+b)$. The resulting representation of the E-k diagram, shown in figure ( ), is referred to as the reduced zone representation.

The E–k curve in the extended zone scheme is figure above has discontinuities at $k = n\pi/(a+b)$ where $n = \pm 1, \pm 2$, etc.. These k-values give the boundaries of the Brillouin zone. As $k = 2\pi/\lambda$, the Brillouin zone boundaries are defined in terms of λ by $2(a+b) = n\lambda$, which is Bragg's law of reflection for normal incidence. Thus the discontinuitites in the E-k curves are associated with the Bragg reflection of the de-Broglie waves representing the electrons for these k-values.

• EFFECTIVE MASS OF ELECTRON:

It is known that electron has a well defined mass and when accelerated by an electric field, it obeys newtonian mechanics. What happens when the e^- is to be accelerated inside a crystal? How will it react to an electric field? The mass of an electron in a crystal appears, in general different from the e^- mass and is usually referred to as the effective mass. The velocity of the e^- in a one dimensional lattice is described by its group velocity given by the equation.

$$v = \frac{d\omega}{dk} \quad \Rightarrow \quad v = \frac{1}{\hbar}\frac{dE}{dk} \qquad \ldots (1)$$

$$\therefore \quad \text{acceleration } a = \frac{dv}{dt} = \frac{1}{\hbar}\frac{d}{dt}\left(\frac{dE}{dk}\right) = \frac{1}{\hbar}\frac{d}{dk}\left(\frac{dE}{dk}\right)\frac{dk}{dt}$$

$$\Rightarrow \quad a = \frac{1}{\hbar}\frac{d^2E}{dk^2}\frac{dk}{dt} \qquad \ldots (2)$$

Now we will find the value of $\frac{dk}{dt}$ under the influence of an applied field E.

Let an e^- be subjected to the influence of an external field of strength ε for a time dt. If the velocity of the e^- is v, the distance travelled in a time dt is vdt.
So, that

$$dE = e\varepsilon\, vdt \quad . \qquad \Rightarrow dE = e\varepsilon\frac{1}{\hbar}.\left(\frac{dE}{dk}\right)dt$$

$$\Rightarrow \quad \frac{dk}{dt} = \frac{e\varepsilon}{\hbar} \qquad \ldots (3)$$

Putting (3) in equation (2) we get

$$a = \frac{1}{\hbar}\frac{d^2E}{dk^2}\left(\frac{e\varepsilon}{\hbar}\right) \qquad \Rightarrow \qquad a = \frac{1}{\hbar^2}e\varepsilon\left[\frac{d^2E}{dk^2}\right] \qquad \ldots (4)$$

Compering this formula with that for a free, classical particle,

$$m\left(\frac{du}{dt}\right) = e\varepsilon \quad \Rightarrow \qquad \frac{dv}{dt} = a = \frac{e\varepsilon}{m} \qquad \ldots (5)$$

$\therefore$ From (4) and (5), we get

$$\boxed{m^*_{(\text{effective mass})} = \frac{\hbar^2}{\left(d^2E/dk^2\right)}} \qquad \ldots (6)$$

So as to write in all case,

$$\boxed{a = \frac{e\varepsilon}{m^*}} \qquad \ldots (7)$$

So, equation (6) indicate, that the effective mass is determined by d^2E/dk^2. It can really shown that for a free e^-

$m^* = m$ because

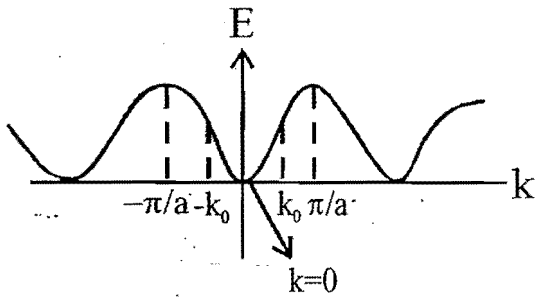
$$E = \frac{\hbar^2k^2}{2m} \;\&\; m^* = \frac{\hbar^2}{d^2E/dk^2}$$

But for an e^- moving in a periodic potential E does not vary with k in the above manner (i.e. curve E vs k is not a parabolic) and So, $m^* \neq m$. So, we can conclude that all the results of the free e^- theory are those provided in m in each case is replaced by suitable m^*. Thus

$$E = \frac{\hbar^2k^2}{2m^*}$$

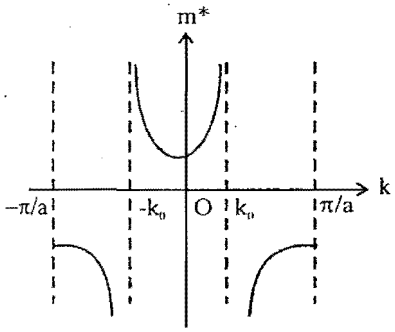
This is known as effective mass approximation.

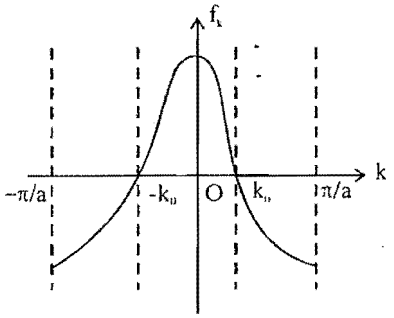
• **Variation of effective mass (m*) with k:**



at $k=0$, E is minimum $\Rightarrow$ $\dfrac{d^2E}{dk^2}=+ve$ $\Rightarrow$ $m^*=+ve$ finite

at $k=\pm\pi/a$ $E=E_{max}$ $\Rightarrow$ $\dfrac{d^2E}{dk^2}=-ve$ $\Rightarrow$ $m^*=-ve$





and the degree of freedom of an e^- is:

$$f_k=\frac{m}{m^*}=\frac{m}{\hbar^2}\left[\frac{d^2E}{dk^2}\right]$$

Example: Taking the origin at the bottom of the conduction band, calculate the crystal momentum for a free electron of energy 0.02 eV. Given, effective mass of the electron = $0.2\ m_0$.

Soln. Taking the origin at the bottom of the conduction band, the energy (E) versus the wave vector (k) relationship is $E=\dfrac{\hbar^2k^2}{2m^*}$.

Here, $E=0.02\ eV=0.02\times1.6\times10^{-19}\ J$ and $m^*=0.2\ m_0=0.2\times9.11\times10^{-31}\ kg$

Hence, crystal momentum $=\hbar k=\left(2m^*E\right)^{1/2}=\left(2\times0.2\times9.11\times10^{-31}\times0.02\times1.6\times10^{-19}\right)^{1/2}$

$$=3.416\times10^{-26}\ kg.m/s$$

Example: The intrinsic carrier concentration of germanium at room temperature is $2.5\times10^{19}\ m^{-3}$. It is doped with phosphorus at a rate of 1 phosphorus atom per million atoms of germanium. If the concentration of germanium. If the concentration of germanium atoms is $5\times10^{28}\ m^{-3}$, calculate the hole concentration. Assume complete ionization of phosphorus atoms.

Soln. The number of phosphorus atoms $= \frac{5\times10^{28}}{10^{6}}\ m^{-3} = 5\times10^{22}\ m^{-3}$. For complete ionization, the concentration of electrons is $n = 5\times10^{22}\ m^{-3}$.

We have $np = n_i^2$ where n_i is the intrinsic carrier concentration. Therefore, the hole concentration,

$$p = \frac{n_i^2}{n} = \frac{\left(2.5\times10^{19}\right)^2}{5\times10^{22}}\ m^{-3} = 1.05\times10^{16}\ m^{-3}$$

Example: Show that the fractional increase in the intrinsic carrier concentration of Si at room temperature increases by 8% per degree rise of temperature.

Soln. The intrinsic carrier concentration is given by

$$n_i = CT^{3/2}\, e^{-E_g/(2k_BT)} \qquad \text{... (i)}$$

where 'C' is a constant. The band gap Eg decreases linearly with temperature obyeing the relationship $E_g = E_{g0} - \alpha T$, where E_{g0} is the energy gap at 0K. Substituting this relationship into (i), we obtain

$$n_i = C'T^{3/2}\, e^{-E_{g0}/(2k_BT)} \qquad \text{... (ii)}$$

where C' is a new constant. Logarithmic differentiation of equation (ii) shows that the fractional increase in n_i is given by

$$\frac{\delta_{n_i}}{n_i} = \left(\frac{3}{2} + \frac{E_{g0}}{2k_BT}\right)\frac{\delta T}{T}$$

For Si, $E_{g0} = 1.21\ eV$. At room temperature (T = 300K), we have $k_BT = 26\ meV = 26\times10^{-3}\ eV$. So, for Si at 300K with $\delta T = 1K$, we obtain

$$\frac{\partial n_i}{n_i} = \left(\frac{3}{2} + \frac{1.21}{0.052}\right)\frac{100}{300}\% = 8\%$$

Example: Silicon contains 5×10^{28} atoms per m^3. In an n-type Si sample and the donor concentration is 1 atm per 2.5×10^{7} Si atoms. Assuming that the electron effective mass is equal to the true mass, calculate the temperature at which the Fermi level lies at the bottom of the conduction band.

Soln. The donor concentration is $N_D = \frac{5\times10^{28}}{2.5\times10^{7}} = 2\times10^{21}\ m^{-3}$

Also, $n_0 = 4.82\times\left(\frac{m_e}{m_0}\right)^{3/2} T^{3/2} = 4.82\times10^{21}\, T^{3/2}$

(Since, $m_e = m_0$). The fermi level is $E_F = E_C - k_BT\ell n\left(\frac{n_c}{n_D}\right)$

Since, $T \neq 0$, $E_F = E_C$ when $n_C = N_D$, i.e.,

$$4.82\times10^{21}\, T^{3/2} = 2\times10^{21}$$

whence, T = 0.56 K

Example: The energy wave vector dispersion relation for a one-dimensional crystal of lattice constant 'a' is given by $E(k) = E_0 - \alpha - 2\beta \cos ka$, where E_0, α, β are constants.

(i) Find the value of 'k' at which the velocity of an eelctron is a maximum

(ii) Find the difference between the top and the bottom of the energy band.

(iii) Obtain the effective mass m^* of the electron at the bottom and at the top of the band.

Soln. (i) The velocity of an electron is $v = \frac{1}{\hbar}\frac{dE}{dk} = \frac{2\beta a}{\hbar}\sin ka$

'v' is a maximum when $\sin ka = 1, \Rightarrow ka = \frac{\pi}{2} \quad \Rightarrow k = \frac{\pi}{2a}$

(ii) At the top of the band E(k) is a maximum, and so $\cos ka$ is a minimum, i.e. $\cos ka = -1$.

So, $E_{top} = E_0 - \alpha + 2\beta$

At the bottom of the band E(k) is a minimum, i.e. $\cos ka$ attains a maximum value of +1. Hence

$$E_{bot} = E_0 - \alpha - 2\beta$$

The difference in energy is, $E_g = E_{top} - E_{bot} = 4\beta$

(iii) $m^* = \frac{\hbar^2}{d^2E/dk^2} = \frac{\hbar^2}{2\beta a^2 \cos ka}$

At the bottom of the band, $\cos ka = 1$; so $m^* = \frac{\hbar^2}{2\beta a^2}$

At the top of the band, $\cos ka = -1$; so $m^* = -\frac{\hbar^2}{2\beta a^2}$

Example: The concentration of ionized donor and acceptors in an n-type compensated semiconductor at temperature T are N_D and N_A respectively. If n_i is the intrinsic carrier concenration at that temperature, show that the concentreation at that temperature, show that the concentration of free electrons and holes in the semiconductor are

$$n = \frac{1}{2}(N_D - N_A) + \frac{1}{2}\sqrt{(N_D - N_A)^2 + 4n_i^2}$$

$\Rightarrow$ $$p = -\frac{1}{2}(N_D - N_A) + \frac{1}{2}\sqrt{(N_D - N_A)^2 + 4n_i^2}$$ respectively.

Soln. As the semiconductor is electrically neutral, we have

$$N_D + p = N_A + n \qquad \ldots (i)$$

For an n-type semiconductor, $N_D > N_A$. Also, $p = n_i^2/n$, so, equation (i) becomes.

$$N_D + \frac{n_i^2}{n} = N_A + n \quad \Rightarrow \quad n^2 - (N_D - N_A)n - n_i^2 = 0$$

$\Rightarrow$ $$n = \frac{1}{2}(N_D - N_A) \pm \frac{1}{2}\sqrt{(N_D - N_A)^2 + 4n_i^2}$$

Since 'n' is positive, the negative sign on the right-hand side must be rejected. Hence

$$n = \frac{1}{2}(N_D - N_A) + \frac{1}{2}\sqrt{(N_D - N_A)^2 + 4n_i^2}, \quad \text{proved}$$

Similarly, putting $n = n_i^2 / p$ on the right-hand side of equation (i) and proceeding in the same way, we obtain

$$p = -\frac{1}{2}(N_D - N_A) + \frac{1}{2}\sqrt{(N_D - N_A)^2 + 4n_i^2}$$

Example: For a solid T.B.A expression is given by

$$E(K) = E_0 - C\cos(K_x a)\cos(K_y a)$$

(a) Expand E(K) (b) bandwidth of the band

(c) Density of states near (0, 0) (d) Effective mass at $(o, \pi/a), (0, 0)$

Soln: $E = E_0 - C\cos(k_x a)\cos(k_y a)$.

Lattice parameter = 2a

For rhomic dodecahedron, (for fcc to bcc)

top of bond from cubic $\left(\frac{2x}{a}, 0, 0\right)\Big/\left(0, \frac{2x}{a}, 0\right)\Big/\left(0, 0, \frac{2x}{a}\right)$, when lattice parameter is a.

For $2-D$, $(\pi/a, 0)$ or $(0, \pi/a)$ top of band

(a) $E = E_0 - C$

(b) $E_{top} = E_0 - C \quad (1, 0)$ $\qquad E_{bottom} = E_0 - C \quad (0, 0)$

$\therefore \quad E = 2C$

(c) $E = E_0 - C\left\{\left[1 - \frac{k_x^2 a^2}{2}\right]\left[1 - \frac{k_y^2 a^2}{2}\right]\right\}$

$$= E_0 - C\left[1 - \frac{k_y^2 a^2}{2} - \frac{k_x^2 a^2}{2} + \frac{k_x^2 k_y^2 a^4}{4}\right] \text{ near } (0, 0)$$

$$= E_0 - C\left[1 - \frac{1}{2}a^2\left(k_x^2 + k_y^2\right)\right] = E_0 - C\left[1 - \frac{k^2 a^2}{2}\right] = E_0 - C + C\frac{K^2 a^2}{2}$$

$$\frac{dE}{dK} = Ca^2K$$

$$\therefore \quad D(E) = 2\left(\frac{L}{2\pi}\right)^2 \frac{1}{Ca^2K} = \frac{2L^2}{4\pi^2 Ca^2K} = \frac{A}{2\pi^2 a^2 CK}$$

(d) $m^*(0, \pi/2) =$ top of bond

$$\frac{d^2E}{dK^2} = Ca^2$$

$$m^* \text{ at top} = \frac{-\hbar^2}{Ca^2}. \quad \text{and} \quad m^*(0, 0) = \frac{\hbar^2}{Ca^2}$$

Example: The energy bond relation in a linear chain with interatomic distance 'a' is given by.

$$E(K) = E_0 - T\cos ka$$

When width of this bond is increased by 20%, calculate the % change in the effective mass of the electron at the bottom of the bond.

Soln. $E(k) = E_0 - T\cos ka$

$$v_g = \frac{1}{\hbar}\frac{dE}{dk} = \frac{Ta\sin ka}{\hbar}$$

$$D(E) = \not{2}\,\frac{L}{\not{2}\lambda Ta\sin Ka} = \frac{L}{T\pi a\sin Ka}$$

$$\frac{d^2E}{dK^2} = Ta^2\cos Ka \quad \Rightarrow m^* = \frac{\hbar^2}{Ta^2\cos Ka}$$

$E_{top} = E_0 + T$ and $E_{bottom} = E_0 - T$

$\therefore \Delta E = 2T.$

$$m^* = \frac{2\hbar^2}{\Delta E a^2 Ka}$$

$$\Rightarrow \ell n\, m^* = \ell n 2 + \ell\hbar^2 - \ell n(\Delta E) - \ell n(a^2) - \ell n(\cos Ka)$$

$$\Rightarrow \frac{1}{m^*}dm^* = 0 + 0 - \frac{1}{\Delta E}d(\Delta E) - 0 - 0 \Rightarrow \frac{dm^*}{m^*} = -\frac{d(\Delta E)}{\Delta E}$$

$$\Rightarrow \frac{dm^*}{m^*}\times 100 - \frac{d(\Delta E)}{\Delta E}\times 100 \Rightarrow \frac{dm^*}{m^*}\times 100 = 20\%$$

i.e., band width increases 20%, m* decreases by 20%

Chapter-4: PHYSICS OF SEMICONDUCTOR

• Energy bands in a solid:

In case of a solid the atoms are arranged in systematic space lattice and hence atom is greatly influenced by neighbouring atoms. Due to this closeness of atoms electrons will be intermixed with neighbouring atoms. Due to this intermixing number of permissible energy levels increases and there are significant changes in the energy levels. So in case of solid instead of single energy levels there will be bands of energy levels associated with single atom. A set of such closely packed energy levels is called an energy band.

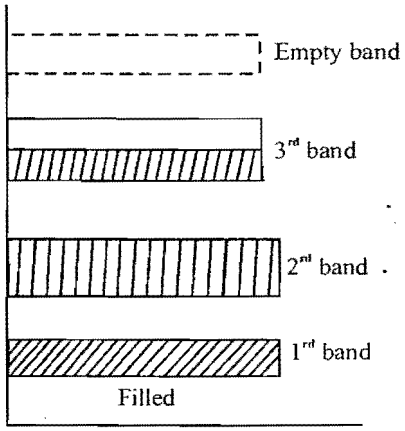
• Concept of energy band formation:

Energy levels of a single isolated atom of silicon is shown in figure.

$$Si(14) \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^2 3d^0$$

Each Silicon atom has 14 electrons two of which occupy K-shell 8 occupy L-shell and 4 occupy M-shell. Two electrons of M shell are in shub-shell 3s and two are in sub shell 3p i.e. 3p sub shell is half filled because it can accommodate a total of 6 electrons.

If many atoms of Silicon are in one solid, then these K-shells differ in extremely small amounts of energy and are merged together and form to merge into one energy band.



Energy band in solid state

• Valence band conduction band and Forbidden band:

1. Valence band: The electrons in outermost shell are called valance electrons. The band formed by a series of energy levels containing valance electrons is known as valance band. This is the highest energy occupied band. Valance band may be partially or completely filled and can never be empty.

2. Conduction band: In certain materials valance electrons are loosely attached to the nucleus. These valance's leave the valance bands and eneter into a band known as conduction band. This is defined as lowest unfilled energy band. The band may be empty or partially filled. If conduction band does not have electrons then current conduction is not possible.

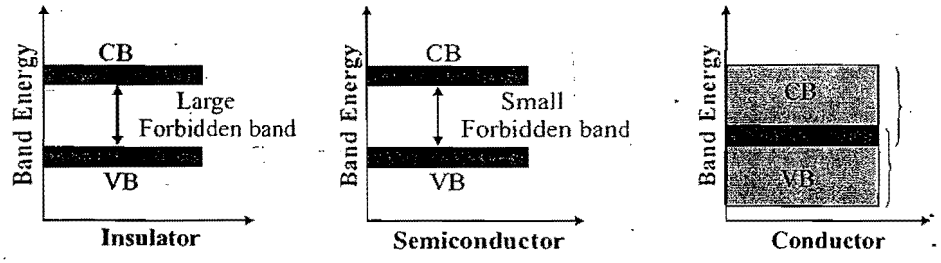
3. Forbidden band: Separation between CB and VB is known as forbidden energy gap. There is no allowed energy state in this gap and hence no electron can stay in forbidden energy gap. Greater is the energy gap means more tightly the valance electrons are bound to nucleus.

• Insulator, Semi-conductors and conductors:

1. Insulator: Forbidden energy band is wide and electrons from VB cannot jump into CB. It is of the order of 10eV at T = 0° K all electrons will be in VB. The resistivity of insulator is of the order of 10^7 Ω-meter.

2. Semi-conductor: Semiconductor material is one whose electrical conductivity lies between insulators and good conductors. Generally energy gap is of the order of 1 eV. At T = 0°K, there are no electrons in conduction band and VB is completely filled. When a small amount of energy is applied then electrons can move easily from VB to CB. If temperature is increased then forbidden band is decreased.

3. Conductors: In this case forbidden band is absent and VB and CB overlap each other. Due to overlapping of VB and CB, a slight potential difference across the conductor causes the free electrons to constitute electric current. Due to absence of forbidden band there is no structure to establish holes and total current is simply flow of electrons.

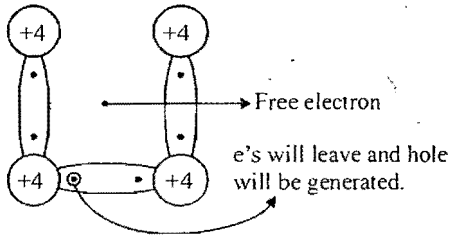


• Conductivity of a semi-conductor:

Materials like Ge and Si have resistivity of order of 10^{-4} to 0.5 ohmmeter. Conductivity of a semi-conductor increases with increase in temperature, i.e. Resistivity will decrease with increase in temperature. So, Semiconductors have negative temperature coefficient of resistance.

• Effect of temperature on Semi-conductor:

At T = 0°K, Semi-conductor crystal behaves as a perfect insulator because covalent bands are very strong and no free electrons are available. At T = 0° K VB is filled but no electron can reach CB to become free electron. At room temperature some of the covalent bonds are broken due to the thermal energy supplied to crystal, and due to the breaking of the bonds, some electrons become free which were engaged in formation of these bands.



• Effect of temperature on E_G:

For Si : $E_G(T) = 1.21 - 3.6\times10^{-4}\,T$

Where T is in 0°K.

At T = 0°K → E_G = 1.21 eV

T = 25°C → E_G = 1.1 eV

For Ge : $E_G(T) = 0.785 - 2.2\times10^{-4}\,T$

At T = 0°K → E_G = 0.785 eV

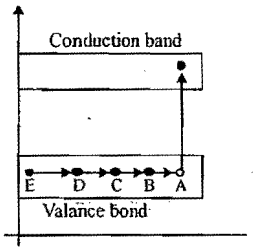
T = 25°C → E_G = 0.72 eV

So, at room temperature energy required to break the covalent bond is 0.72 eV for Ge and 1.1 eV for Si. So, at room temperature electrons move from VB to CB.

• Concept of holes:

At room temperature when covalent bonds are broken then leaves the vicinity of an atom and leaves a +ve charge behind this positive charge is called hole. So hole is the nothing but missing electron in the covalent bond.

Due to thermal energy an electron leaves the VB and enter into conduction band. This electron leaves a vacancy in valance band at A. Now valance electron B, comes at A to fill hole at A. This process is repeated and valance electron move along path EDCBA while hole move along the path ABCDE. Here hole current is due to the movement of valance electrons from one covalent band to another covalent band. The conductivity of Ge increasing by about 6% per degree increasing in temperature. While in Si it is about 8% degree increasing in temperature.

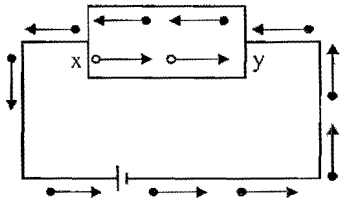


• Types of Semi-conductors:

1. Intrinsic semi-conductor:

It is an extremely pure form of Semi-conductor in which electrons and holes are created by thermal excitation. The electrons reaching the CB due to the thermal excitation leave equal number of valancies or holes in VB. In case of intrinsic S.C. No. of free e's is always equal to number of holes.

Current flow in intrinsic - Semi conductor:



When an extemal field is applied across an intrinsic semi-conductor then conduction through semiconductor is by both electrons and holes.

Free electrons in CB move towards the +ve terminal of battery while holes in VB move towards negative terminal of battery. So total current inside the S.C is sum of currents due to both electrons and holes. Current in external wire is due to electrons only and due to holes. When holes reach at negative terminal y then e's reaching here combine with holes and these holes are destroyed. Now again new holes are created and process is continued.

2. Extrinsic semiconductor:

The electrical conductivity of intrinsic semiconductor can be increased by adding some impurity in process of crystallization. The added impurity is very small of the order of one atom per million atoms of pure semiconductor.

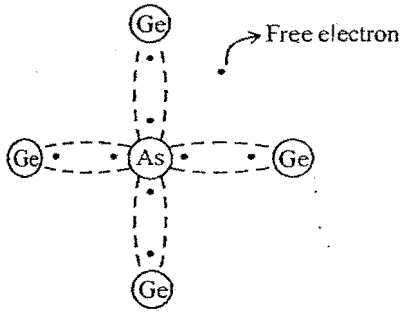
However the increase in conductivity by addition of minute impurities is about 20 times.

Types of extrinsic Semi-conductor:

(A) N-type: When doping material is pentavalent atoms e.g Bi, Sb, As and P.

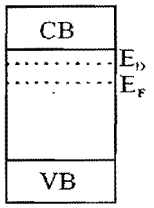
This atom is known as donor atom because it donates one electron to CB of pure, semiconductor.

When a small amount of pentavalent impurity is added to a pure semiconductor cyrstal during crystal growth, the resulting erystal is known as N-type extrinsic semiconductor.



Arsenic atom fits in Ge crystal in such a way that its four valance electrons form covalent bonds with 4, Ge atoms. 5th electron of As atom is not covalently bonded but it is loosely bound to parent Arsenic atom. The amount of energy needed to detach this 5th valance electron from impurity atom is of the order of only 0.01 eV for Ge and 0.05 eV for Si. This energy is very small and may be provided with thermal agitation at room temperature. Such a liberated valance electron is then free to move in a cuptal lattice in same way as free electrons in an intrinsic semiconductor. So, by addition of pentavalent atom the concentration of electrons in CB is increased. When pentavalent electron gives one electron then as at on becomes positively charged ion. This Arsenic atom cannot take part in conduction because it is firmly fixed into crystal lattice.

Fifth left over valance electron is not accommodated in VB, but moves to CB. Although each Arsenic atom provides only one free electron, yet an extremely amount of arsenic impurity provides enough atoms to supply millions of free electrons.



N-type Semi-conductor

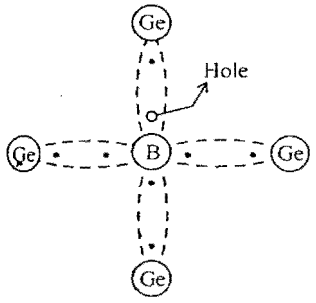
• Important points about N-type Semiconductor:

(i) No. of e's > No. of hole.

(ii) It is electrically neutral, because extra electrons are created by addition of neutral pentavalent impurity atoms to ms to Semi-conductor. So no extra +ve or –ve charge is added.

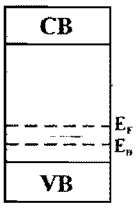
(iii) When N-type semiconductor is placed between two electrodes and an electric field is applied then excess electrons donated by impurity atoms will travel towards the positive electrode. This constitutes the electric current.

(B) P-type: When doping material is tri-valent atoms such as Ga, In, Al and B (Which have three valance electrons). This trivalent is known as acceptor atom because it accepts one electron from semi-conductor atoms.



When boron is added to Ge then each atom of boron fits into Ge crystal with only three covalent bonds. Here 3 valance electrons of boron atom form covalent bonds with valance electrons of Ge atom. For fourth covalent bond one valance electron will care from Ge and there is deficiency of one electron which is called hole.

So for each boron atom added, one hole is created, a small amount of boron provides million of holes.



Impurity atoms are called acceptor because they accept electrons Ge atoms. Since current carriers are positively charged particles (holes). This type of S.C. is a P-type S.C.

• Important points about P-type semi-conductors:

(i) No. of holes > No. of electrons.

(ii) P-type semiconductor remains electrically neutral as the number of mobile holes under all conditions remains equal to no. of acceptors.

(iii) When an electric field is applied the current conduction is predominantly by holes. Holes are positively charged they are directed towards negative terminal and constitute the hole current. In P-type valance electrons move from one covalent bond to another covalent bond.

Charge neutrality in a semi-conductor:

Let n and p are electrons and hole concentration respectively and n_i is intrinsic concentration. If N_D be the concentration of donor atoms. As donor atoms are ionized at room temperature then there will be N_D immobile positive charges per cubic meter contributed by donor ions. So, total positive charge be $(N_D + p)$ if N_A be the concentration of acceptor atoms. In this case there will be N_A immobile negative charges per cubic meter. So, total negative charge will be $(N_A + n)$.

But semi-conductor is neutral so

$$\boxed{n + N_A^- = N_D^+ + p}$$

• Mass action law:

Under thermal equilibrium the product of concentration (n) of free electron and concentration (p) of holes is constant.

It is independent of the amount of doping by donor and acceptor impurities.

Here $n.p = n_i^2$ is called Mass-action law.

This law is valid for both intrinsic and extrinsic semiconductors.

Where $n_i^2 = A_0 T^3 \, e^{-(E_G/kT)}$

Charge density in N and P-Type semi-conductor.

(A) N-Type:

$$n + N_A^- = N_D^+ + p$$

For N-Type there is no acceptor doping.

So, $N_A^- = 0$ and n >> p

So, $n \simeq N_D^+$

So, in N-type free electron concentration is approximately equal to density of donor atoms.

$$n.p = n_i^2 \quad \Rightarrow \quad \boxed{p = \frac{n_i^2}{N_D^+}}$$

(B) **P-Type:**

$n + N_A^- = N_D^+ + p$

For P-type there is no donor doping so, $N_D^+ = 0$ & $p >> n$

So, $\boxed{p = N_A^-}$

So in case of P-type hole concentration is approximately equal to density of acceptor atoms.

$$n.p = n_i^2 \quad \Rightarrow \quad \boxed{n = \frac{n_i^2}{N_A^-}}$$

Example: If relative density of tungeston is 18.8 gm/cm^3 and its atomic weight is 184 assuming that at room temperature there are two free electrons per atom, calculate the density of free electrons n.

Soln. Let volume = 1 cm^3.

So, Weight = 18.8 gm for 1 cm^3 volume.

$\because$ 184 gm tungsten has 6.02×10^{23} atoms or $2\times6.02\times10^{23}$ electrons.

$\therefore$ 1 gm tungsten has $\frac{2\times6.02\times10^{23}}{184}$ electrons.

$\therefore$ 18.8 gm/cm^3 tungsten has $\frac{2\times6.02\times10^{23}}{184}\times18.8\ e's/cm^3$

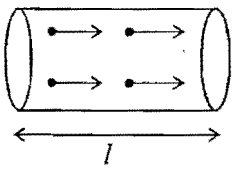
So, here no. of free electrons $= 1.23\times10^{23}\ e's/cm^3$

• Ohm's law for conduction current:

$J = \sigma E$ is ohm's law for conduction current.

Let n is number of electrons per cm^3 and N is total number of electrons per cm^3.

$$N = n.q$$



Let A is area of cross section and ℓ is length of conductor then total charge

$$Q = n.q.A.\ell$$

Let electrons move with velocity V_d then total time to travel $T = \frac{\ell}{v_d}$

So, total current = $I = \frac{Q}{T} = \frac{nqA\ell}{\ell}.v_d$

Current density $(J) = \frac{I}{A} = nqv_d = nq\mu E$

If $\sigma = nq\mu \quad \Rightarrow \quad \boxed{J = \sigma E}$

Conductivity of N-type is $\sigma_n = nq\mu_n$

Conductivity of P-type is $\sigma_p = pq\mu_p$

•Conductivity:

Conductivity of a metal is different from conductivity of a semiconductor. In case of N-type semiconductor conduction is by electrons while in P-type semiconductor conduction is by holes. For intrinsic semiconductor conductivity depends upon both electrons and holes.

1. Conductivity of intrinsic semiconductor:

$$\sigma_i = nq\mu_n + pq\mu_p$$

For intrinsic S.C. $n = p \quad \Rightarrow \quad \boxed{n = p = n_i}$

So, $\sigma_i = n_i q\left(\mu_n + \mu_p\right)$

Resistivity of intrinsic S.C. is $\rho_i = \dfrac{1}{n_i q\left(\mu_n + \mu_p\right)}$

2. Conductivity of N-type semi-conductor:

$\sigma_n = nq\mu_n$ for N-type $\qquad \boxed{n = N_D^+}$

$\sigma_n = N_D^+ . q . \mu_n \left(n >> p\right)$

3. Conductivity of P-type semi-conductor:

$\sigma_p = pq\mu_p$ for P-type $\qquad \boxed{p = N_a^-}$

$\sigma_p = N_a^- . q . \mu_p \quad (\mathrm{p} >> \mathrm{n})$

Example: Calculate the conductivity of pure silicon at room temperature when concentration of carriers is 1.6×10^{10} *per* cm^3. Take $\mu_n = 1500\ cm^2$ / v sec and $\mu_p = 500\ cm^2$ / v sec at room temperature.

Soln. $\sigma_i = qn_i\left(\mu_n + \mu_p\right)$

$\sigma_i = 1.6\times10^{-10}\times1.6\times10^{10}\times2000 \quad \Rightarrow \sigma_i = 5.12\times10^{-16}\ Mho/cm$

Example: If mobilities of electrons holes in a sample of intrinsic Ge at room temperature are 0.36 m^2/v sec and 0.17 m^2/v sec respectively. If the electron and hole densities are each equal to 2.5×10^{-19} *per* m^3. Calculate Ge resistivity.

Soln. **For intrinsic S.C.**

$$\sigma_i = qn_i\left(\mu_n + \mu_p\right)$$

$$\sigma_i = 1.6\times10^{19}\times2.5\times10^{-19}\times\left(0.36+0.17\right)$$

$$\sigma_i = 2.12 \text{ Simens/meter}$$

So, $\rho_i = 0.47$ ohm-meter

Example: For an intrinsic silicon at 300°K it is given that n_i value is 1.5×10^{10} per cm^3. If donor type impurity is added to extent of 1 impurity atom in 10^8 silicon atoms then calculate the value of conductivity after doping. If $\mu_n = 1300\ cm^2/V$ sec $\mu_p = 500\ cm^2/$v sec.

Soln. In case of Si no. of atoms/cm^3 = 5×10^{22} if there is 1 donor atom per 10^8 silicon atoms.

then $N_D = \dfrac{5\times10^{22}}{10^8} = 5\times10^{14}$ atoms/cm^3

So, conductivity of N-type is

$$\sigma_n = N_D.q.\mu_n = \frac{5\times10^{14}}{cm^3}\times1.6\times10^{-19}\ C\times\frac{1300\ cm^2}{\text{v sec}} \Rightarrow \sigma_n = 0.104\ (mho/cm)$$

Example: If mobility of free electron and holes in pure Ge are 0.38 and $0.18\ m^2/V$ sec. The corresponding values for pure silicon are 0.13 and 0.05 respectively. Compare value of intrinsic resistivity for both the materials.

Soln. $Ge:\rightarrow$ $\sigma_i = n_i\ q(\mu_n + \mu_p)$

$\sigma_i = 2.5\times10^{19}\times1.6\times10^{-19}\times(0.56) \Rightarrow \sigma_i = 2.24$ Mho/meter

$Si:\rightarrow$ $\sigma_i = 1.5\times10^{16}\times1.6\times10^{-19}\times0.18 \Rightarrow \sigma_i = 0.432\times10^{-3}$ Mho/meter

$\dfrac{\sigma_{Ge}}{\sigma_{Si}} = (5185)$

Example: Calculate the number of atoms/cm^3 in case of Ge and Si.

For Ge: Atomic wt. = 72.6
Density = 5.32 gm/cm^3.

For Si: Atomic wt = 28.1
Density = 2.33 gm/cm^3.

Soln. $Ge:\rightarrow$ 72.6 gm has 6.02×10^{23} atoms

5.32 gm/cm^3 has $\dfrac{6.02\times10^{23}}{72.6}\times5.32\ atoms/cm^3$

$= 4.41\times10^{22}\ atoms/cm^3$

$Si:\rightarrow$ 28.1 gm has $6.02\times10^{23}\ atoms$

2.33 gm/cm^3 has $\dfrac{6.02\times10^{23}}{28.1}\times2.33\ atoms/cm^3$

$= 5\times10^{22}\ atoms/cm^3$

• Variation of mobility w.r.t. electric field:

1. If $E < 10^3$ v/cm then $\mu \rightarrow$ constant

2. If 10^3 v/cm < E < 10^4 v/cm then $\mu \propto E^{-1/2}$.

3. If $E > 10^4$ v/cm then $\mu \propto E^{-1}$.

For low value of electric field mobility is constant but for higher value of electric field mobility is inversely proportional to electric field.

FERMI LEVEL

• The Fermi-Dirac distribution:

The equation for f(E) is called the Fermi Dirac probability function and specifies the fraction of all states at energy E(electron volt) occupied under conditions of thermal equilibrium f(E) is defined as

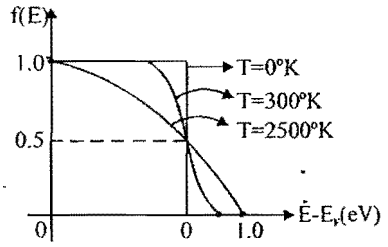
$f(E)=\frac{1}{1+e^{(E-E_F)/kT}}$ Where K is Boltzmann constant in eV/°K and T is temperature in °K.

E_F is Fermi level or characteristic energy for crystal in eV.

• Definition of E_F:

The Fermi level represents the energy state with 50% probability of being filled if no forbidden band exists. So, If $E = E_F$ then $f(E) = 1/2$ for any value of temperature.

• Plot of f(E) v's $E-E_F$(eV):



When T = 0°K:

Case 1: If $E > E_F$ then exponential term becomes infinite and f(E) = 0. Consequently there is no probabilities of finding an occupied quantum state of energy greater than E_F at absolute zero.

Case 2: If $E < E_F$ then exponential term becomes zero and f(E) = 1. All quantum levels with energies less than E_F will be occupied at T = 0°K.

• Energy Density:

$dn_e = \rho_E dE$ ... (1)

dne → No. of free e's per cubic meter whose energies lie in internal dE.

ρ_E → Density of electrons, i.e. no. of e's per electron volt per cubic meter of metal.

But $\rho_E = f(E)N(E)$ ... (2)

$N(E)$ → Density of states i.e No. of states per electron volt per cubic meter in conduction band

$f(E)$ → Probability that a quantum state with energy E is occupied by an electron.

The expression N(E) is given by $N(E) = \gamma E^{1/2}$ ... (3)

Where γ is a constant.

$$\gamma = \frac{4\pi}{h^3}(2m)^{3/2}\left(1.6\times10^{-19}\right)^{3/2} = 6.82\times10^{27}\left(m^{-3}\right)(eV)^{-3/2}$$

• Energy distribution in a metal:

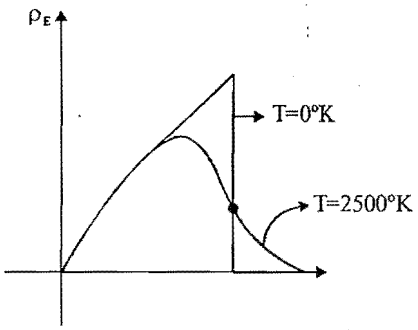
$\rho_E = \gamma E^{1/2}$ For $E < E_F$ this relationship is known as completely degenerate energy distribution function.

$= 0$ For $E > E_F$

Fermi energy is the maximum that any electron may posses at absolute zero. Fact that the electrons actually have energies extending from 0 to E_F at absolute zero is a consequence of Pauli exclusion principle which state that no two electron may have the same set of quantum numbers. Hence not all electrons can have the same energy even at 0°K.

• Plot of ρ_E versus E:

The distribution function changes only very slightly with temperature even though the temperature is as great at 2500°K. The effect of high temperature is merely to give those electrons having the high energies at absolute zero.



• Calculation of Fermi Level:

The area under the curve of given figure represents the total number of free electrons. Thus

$$n = \int_0^{E_F} \gamma E^{1/2} dE = \frac{2}{3}\gamma {E_F}^{3/2} \quad \Rightarrow E_F = \left(\frac{3n}{2\gamma}\right)^{2/3}$$

By putting the value of γ in above expression value of E_F will be

So, $E_F = 3.64 \times 10^{-19}\, n^{2/3}$ where value of n varies from metal to metal and value of E_F is in eV.

For more practical cases value of E_F is less than 10 eV.

• Calculation of number of electrons in conduction band:

$dn = \rho_E dE$

But $\rho_E = f(E)N(E)$

So, $dn = f(E)N(E)dE$

Where dn represents the number of conduction electrons per-cubic meter whose energy lies between E and E+dE the density of states n(E) is derived on the assumption that bottom of conduction band is at zero potential.

In a semiconductor the lowest energy in conduction band is at E_C and so value of N(E) must be:

$N(E) = \gamma (E - E_C)^{1/2}$ for $E > E_C$

Value of number of electrons in conduction band is given by:

$$n = \int_{E_C}^{\infty} N(E) f(E) dE$$

For $E \geq E_C \quad E - E_F >> kT \quad f(E) = e^{-(E-E_C)/kT}$

$$n = \int_{E_C}^{\infty} \gamma (E - E_C)^{1/2} e^{-(E-E_C)/kT} dE = N_C e^{-(E-E_C)/kT}, \qquad \text{Where } N_C = 2\left(\frac{2\pi m_n kT}{h^2}\right)^{3/2}$$

• Calculation of number of holes in valance band:

$N(E) = \gamma (E_V - E)^{1/2}$ for $E < E_V$

Value of number of electrons in conduction band is given by:

$$p = \int_{-\infty}^{E_V} N(E) f(E) dE$$

For $E \leq E_V \quad E_F - E >> kT$ So, $f(E) = e^{-(E_F-E)/kT}$

$$p = \int_{-\infty}^{E_V} \gamma (E_V - E)^{1/2} e^{-(E_F-E)/kT} dE = N_V e^{-(E_F-E)/kT} \quad \text{Where } N_V = 2\left(\frac{2\pi m_p kT}{h^2}\right)^{3/2}$$

• Position of Fermi level in an intrinsic semiconductor:

$n = N_C e^{-(E_C-E_F)/kT}$ & $p = N_V e^{-(E_F-E_V)/kT}$

For an intrinsic semiconductor $n = p$

$$N_C e^{-(E_C-E_F)/kT} = N_V e^{-(E_F-E_V)/kT} \quad \Rightarrow \quad E_F = \frac{E_C + E_V}{2} + \frac{3}{4} kT \ln\left(\frac{m_p}{m_n}\right)$$

For an intrinsic semiconductor if effective mass of both electrons and holes are equal.

Then $N_C = N_V$ so $E_F = \frac{E_C + E_V}{2}$. Hence Fermi level lies in centre of forbidden energy band.

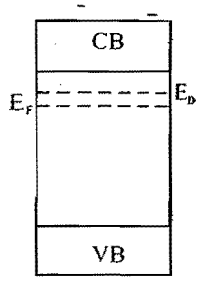
If $m_p > m_n$ then $E_F > \frac{E_C + E_V}{2}$ and if $m_p < m_n$ then $E_F < \frac{E_C + E_V}{2}$

• Position of Fermi level in N-type:

$$n = N_C e^{\frac{E_C - E_F}{kT}}$$

For N-type $n = N_d^+ \quad \Rightarrow \quad E_F = E_C - kT \ln\left(\frac{N_C}{N_D^+}\right)$

• Position of Fermi-level in N-type at room temperature.



At T =0°K Fermi-level is at CB but at room temperature Fermi-level will be just near to CB but below donor level.

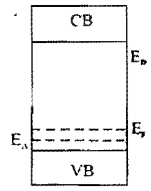
Position of Fermi-level in P-type:

$$p = N_v e^{\frac{(E_F - E_V)}{kT}}$$

For P-type $p = N_A^-$

So, $N_A^- = N_v\, e^{-\frac{(E_F - E_V)}{kT}} \Rightarrow E_F = E_V + kT \ln\left(\frac{N_V}{N_A^-}\right)$

At T = 0°K $\rightarrow E_F = E_V$ but at room temperature Fermi-level we just near to VB but above acceptor level.



• Effect of temperature in N-type and P-type semiconductor:

In case of N and P type by increasing temperature number of electron hole pairs are increased. Ratio of no. of electrons to number of hole (in case of n type) and number of holes to number of electrons (in case of p type) are decreased. So, an extrinsic semiconductor behaves like an intrinsic semiconductor and Fermi-level shifts towards centre of semiconductor.

• Effect of doping on N type and P type semiconductor:

In case of N and P type by increasing doping (degenerate semiconductor) Fermi level shifts inside the CB in case of N type and shifts inside the VB in case of P type. So by increasing doping Fermi level shifts inside the bands.

• Value of intrinsic concentration (n_i):

$$n = N_C e^{-(E_C - E_F)/kT}, \qquad p = N_V e^{-(E_F - E_V)/kT}$$

Here $n.p = n_i^2 = N_C N_V\, e^{-(E_C - E_V)/kT} \Rightarrow n_i^2 = N_C N_V\, e^{-(E_G/kT)}$

Where $N_C = 4.82\times10^{21}\left(\frac{m_n}{m_0}\right)^{3/2} T^{3/2}$ & $N_V = 4.82\times10^{21}\left(\frac{m_p}{m_0}\right)^{3/2} T^{3/2}$

So, $n_i^2 = \left(2.33\times10^{43}\right)\left(\frac{m_n m_p}{m_0^2}\right)^{3/2} T^{3/2}\, e^{-\frac{E_G}{kT}} \Rightarrow n_i^2 = A_0 T^3\, e^{-(E_G/kT)}$

Example: Calculate the probabilities for an electron state to be occupied at 20°C if energy of state lies 0.11 eV above and 0.11 eV below Fermi-level.

Soln. $f(E)=\dfrac{1}{1+\exp(E-E_F/kT)}$

Case 1: $E-E_F=0.11\,eV, \quad \dfrac{kT}{q}=\dfrac{273+20}{11600}=25.2\,mV$

So, $kT=0.0252\,eV$

So, $f(E)=\dfrac{1}{1+e^{\frac{0.11}{0.0252}}}=0.012$

Case 2: $E-E_F=-0.11\,eV$

$$f(E)=\frac{1}{1+\exp\left(\dfrac{E-E_F}{kT}\right)}=\frac{1}{1+\exp\left(\dfrac{-0.11}{0.0252}\right)}, \quad f(E)=0.98$$

Example: What is occupation number at room temperature of an electron state lying 0.1 eV above Fermi-level and 0.1 eV below Fermi-level.

Soln. 0.018, 0.98

Example: Calculate the temperature at which there is 1% probability that a state with an energy 0.5 eV above the Fermi-energy will be occupied by an electron.

Soln. 1264°K.

Example: For an intrinsic S.C. with energy gap of 0.7 eV, calculate position of Fermi-level if $m_p=6m_n$. at room temperature.

Soln. $E_F=\dfrac{E_C+E_V}{2}+\dfrac{3}{4}kT\ln\left(\dfrac{m_p}{m_n}\right)=\dfrac{0.7}{2}+\dfrac{3}{4}(0.026)\ln(6)=0.385\,eV$

Example: In a given N-type Si material if donor concentration is one atom per 2×10^8 silicon atoms. Assuming that effective mass of electron is equal to its true mass. Find the value of temperature at which Fermi-level coincides with the edge of conduction band density of atoms in Si is 5×10^{28} atoms per m^3.

Soln. $N_D=\dfrac{5\times10^{28}}{2\times10^8}=2.5\times10^{20}/m^3$

It is given that $E_F=E_C$

So, $\boxed{N_D=N_C}$

$$N_C=4.82\times10^{21}\left(\frac{m_n}{m_0}\right)^{3/2}T^{3/2}$$

$N_D=2.5\times10^{20}=4.82\times10^{21}\times T^{3/2}$ $\because$ $\boxed{m_n=m_0}$

So, $\boxed{T=0.14^\circ K}$

Example: A Si semiconductor sample at T = 300°K is doped with phosphorus atoms at concentration of 10^{15} cm^3. What is the position of Fermi level with respect to intrinsic Fermi level.

Soln. $E_F - E_{Fi} = kT \ln\left(\frac{N_d}{n_i}\right)$

$$= 0.026\,eV.\ln\left(\frac{10^{15}}{1.5\times10^{10}}\right) = 0.287\,eV$$

Example: A hypothetical semiconductor has an intrinsic carrier concentration of 1.0×10^{10} /cm^3 at 300 K, it has conduction and valence band effective densities of states N_C and N_V both equal to 10^{19}/cm^3.

(a) What is band gap.

(b) If the semiconductor is doped with $N_d = 1\times10^{16}$ donar/cm^3. What are the equilibrium electron and hole concentration at 300 K.

(c) If the piece of semiconductor, already having $N_d = 10$ donar/cm^3 is also doped with $N_a = 2\times10^{16}$ acceptor/cm^3. What are the new equilibrium electron hole concentration.

(d) Consistent with your answer to the part c. What is the fermi level position with respect to the intrinsic fermi level (E_F–F_i).

Soln. (a) $n_i = (N_V N_C)^{1/2}\, e^{-E_g/2kT} \Rightarrow 10^{10} = 10^{19}\, e^{-E_g/2\times0.026eV}$

$10^{-9} = e^{-E_g/0.052eV} \Rightarrow \log\left(10^{-9}\right) = \frac{-E_g}{0.052\,eV}$

$20.72 = E_g / 20.052$ $\boxed{E_g = 1.078\,eV}$

(b) $n_0 p_0 = n_i p_i$ (law of mass action)

$n_0 = N_d = 10^{16}$ (At room temperature)

$p_0 = \frac{n_i^2}{n_0} = \frac{10^{20}\times2.25}{10^{16}} \Rightarrow p_0 = = 2.25\times10^4 / cm^3$

(c) $N_d = 10^{16}$ donor/cm^3, $N_a = 2\times10^{16}$ acc./cm^3, $N_d^+ + p = N_a^- + n$

$10^{16} + p = 2\times10^{16} + n$ $\because$ p_0 dominant

$10^{16} + p_0 = 2\times10^{16}$ n neglected.

$p_0 = 10^{10} / cm^3$

$\boxed{n_0 = \frac{10^{20}}{10^{16}} = 10^4/cm^3}$ It becomes p-type

(d) $p_0 = n_i e^{\frac{E_i - E_F}{kT}}$ ($\because$ consistent to part c)

$\frac{10^{16}}{10^{10}} = e^{\frac{E_i - E_F}{kT}} \Rightarrow 10^6 = e^{\frac{E_i - E_f}{kT}}$

$\Rightarrow 6\times2.303\times0.026 = E_i - E_f \Rightarrow E_i - E_f = 0.36\,eV$

Example: Show that

(a) Minimum conductivity of a semiconductor sample occurs when equilibrium constant electron.

$$n_0 = n_i\sqrt{\frac{\mu_p}{\mu_n}}$$

(b) What is expression for minimum conductivity.

(c) Compare σ_{min} with $\sigma_{instrinsic}$

Soln. Let $\sigma = e\left(n\mu_n + p\mu_p\right)$

$$\sigma = e\left(n\mu_n + \frac{n_i^2}{n_0^2}\mu_p\right) \qquad \therefore \quad \frac{d\sigma}{dn} = 0$$

$$\mu_n - \frac{n_i^2}{n_0^2}\mu_p = 0 \quad \Rightarrow \quad \mu_n = \frac{n_i^2}{n_0^2}\mu_p \quad \Rightarrow \quad n_0^2 = n_i^2\frac{\mu_p}{\mu_n}$$

For min conductivity $\boxed{n_0 = n_i\sqrt{\frac{\mu_p}{\mu_n}}}$ $\boxed{p_0 = n_i\sqrt{\frac{\mu_n}{\mu_p}}}$ Equilibrium conc. min conductivity.

(b) $\sigma_{min} = e\left(n_0\mu_n + p_0\mu_p\right)$

$$e\left(n_i\sqrt{\frac{\mu_p}{\mu_n}}\mu_n + n_i\sqrt{\frac{\mu_n}{\mu_p}}\mu_p\right) \qquad \boxed{\sigma_{min} = n_i\, e\left(2\sqrt{\mu_p\mu_n}\right)}$$

(c) $\sigma_{int} = en_i\left(\mu_n + \mu_p\right)$, $\sigma_{min} = n_i e 2\sqrt{\mu_p\mu_n}$, $\frac{\sigma_{int}}{\sigma_{min}} = \frac{\mu_n + \mu_p}{2\sqrt{\mu_p\mu_n}}$

$$\therefore \quad \boxed{\sigma_{int} = \frac{\mu_n + \mu_p}{2\sqrt{\mu_p\mu_n}}\sigma_{min}}$$

Example: A 0.46 μm thick sample of GaAs is illuminated with monochromatic light of $h\upsilon = 2$ eV, absorption coefficient $\alpha = 5\times10^4$ cm^{-1}. The power incident on the sample is 10 mW. Band gap of material is E_g = 1.43 eV find the total energy absorbed by the sample per second.

Soln. $x = 0.46 = 4.6\times10^{-5}$ cm^{-1}, $h\nu = 2$ eV, $\alpha = 5\times10^4$ cm^{-1}, $E_g = 1.43$ eV

$I_0 = 10$ mW. $\quad \therefore \quad h\upsilon > E_g$

$\therefore \quad I_t = I_0e^{-\alpha x}$

$$= 10\, e^{-5\times10^4\times4.6\times10^{-5}} = 10\, e^{-23.0\times10^{-1}} = 10\times e^{-2.3}$$

Transmit $= 10\times e^{-2.3} = 1.002$

$\therefore \quad$ Absorbed $= I_0 - 10\, e^{-2.3} = 10 - 1.002 = 8.998$ mw

Example: A Si seminconductor is doped with $10^{13}/cm^3$ donar impurity and conduction band edge lies 10 meV above donar level edge at room temperature. Concentration of electrons in semiconductor will be

(a) $10^{15}/cm^3$ (b) $10^{10}/cm^3$ (c) $10^{13}/cm^3$ (d) $2\times10^{11}/cm^3$.

Soln. **(c)**

[**Hint:** At 0K, concentration equal to intrinsics semiconductor].

Example: P-N junction under farward bias barrier potential and depletion region width

(a) Both increases

(b) Both decreases

(c) Barrier potential increases and depletion region width decreases

(d) Barrier potential decreases and depletion region width increases

Soln. **(b)**

Example: Identify the correct statement

(a) Zener and Avalanche breakdown both occurs on heavily semiconductor.

(b) Zener and Avalanche breakdown both occurs on lightly semiconductor.

(c) Zener breakdown occurs on heavily but Avalanche occurs lightly doped seminconductor.

(d) Zener breakdown occurs on lightly semiconductor but avalanche occurs heavily doped semiconductor.

Soln. **(c)**

Example: A semiconductor is doped with B (boron) impurity of concentration 10^{16} atoms/cm^3. What are the concentration of electron and holes (intrinsic carrier conc. is $n_i = 1.5\times10^{10}/cm^3$).

(a) $n = 10^{16}/cm^3$, $p = 2.25\times10^4/cm^3$.

(b) $n = 2.25\times10^4/cm^3$, $p = 10^{16}/cm^3$.

(c) $n = 1.5\times10^{10}/cm^3$, $p = 10^{16}/cm^3$.

(d) $n = 2.25\times10^4/cm^3$, $p = 1.5\times10^{10}/cm^3$.

Soln. **(b)**

Example: A Si solar cell has a short circuited current of 100 mA and open circuit voltage of 0.84 V under full solar illumination. The fill factor is 0.7. What is the max power delivered to a load by this cell.

Soln. $I_{SC} = 100\ mA$

$V_{OC} = 0.8\ V$

$P_{max} = ?$ $\quad \because P_{max} = I_m V_m \text{ (to load)}$

$$\frac{I_m V_m}{I_{SC} V_{OC}} = 0.7 \qquad \Rightarrow \frac{I_m V_m}{100\times0.8} = 0.7$$

$$I_m V_m = 0.7\times100\times0.8 = 56\ mw$$

Example: A photoconductive cell, $1\times1\times1\ mm^3$ Cds crystal is illuminated with light of wavelength 450 nm and intensify

1 mw/cm^2. Assuming quantum efficiency of unity. Calculate the number of electron hole pairs generated per second given the energy band gap of Cds is 2.6 eV.

Soln. $E_g = 2.6\ eV$

$\because \quad I_{op} = g_{op} A_c (L_n + L_p + w)$

$A = 1\ mm^2 = 10^{-2}\ cm^2$

$t = 1\ mm = 0.1\ cm$

Q.E = 1

$P_{in} = ?$ $\quad I_{in}\times A = 10^{-3}\ W/cm^2\times10^{-2}\ cm^2$

$$P_{in} = 10^{-5}\ W.$$

Sensitivity

$$R = \frac{I_{op}}{P_{in}}, \qquad Q.E. = \frac{R \times 1240}{\lambda(nm)} = \frac{I_{op} \times 1240}{P_{in} \times \lambda(nm)} = 1 \quad \Rightarrow \quad \frac{I_{op} \times 1240}{10^{-5} \times 450} = 1$$

$$I_{op} = \frac{10^{-5} \times 450}{1240} = 3.63 \times 10^{-6}\ A = 3.63\ \mu A$$

$$\because \quad I_{op} = eA\, g_{op} t$$

$$3.63 \times 10^{-6} = 1.6 \times 10^{-19} \times 10^{-2} \times g_{op} \times 0.1$$

$$g_{op} = \frac{3.63 \times 10^{-6}}{1.6 \times 10^{-19} \times 10^{-2} \times 0.1}$$

$$\boxed{g_{op} = 2.27 \times 10^{16} / cm^3 - sec}$$

Exmaple: Given that the density of states related effective masses of e^- s and holes in Si are approximately 1.08 m_e and 0.56 m_e respectively, and the electron and hole drift, mobility at room temp are 1350 and 450 $cm^2v^{-1}s^{-1}$ respectively. Calculate the intrinsic concentration and intrinsic resistivity of Si.

Soln. $N_c = 2\left(\frac{2m_n * kT}{h^2}\right)^{3/2}$ and $N_V = 2\left(\frac{2\pi m_p * kT}{h^2}\right)^{3/2}$

$N_C = 2.8 \times 10^{19}\ cm^{-3}$
$N_V = 1.05 \times 10^{19}\ cm^{-3}$

Intrinsic concentration $n_i = (N_C N_V)^{1/2} \exp\left(\frac{-E_g}{2kT}\right) = 1 \times 10^{10}\ cm^{-3}$

Conductivity $\sigma = en_i\mu_n + en_i\mu_p = en_i(\mu_n + \mu_p) = 2.9 \times 10^{-6}\ \Omega^{-1}cm^{-1}$

$\rho = \frac{1}{\sigma} = 3.5 \times 10^5\ \Omega cm$.

Example: Estimate the mean speed of electrons in the conduction bond of Si.

Soln. Average K.E.= $\frac{1}{2} m_e^* v_e^2$ in CB = 3/2 kT.

$V_e = \left(\frac{3kT}{m_e^*}\right)^{1/2} = 2.3 \times 10^5\ ms^{-1}$.

Example: The intrinsic resistivity of Germanium at 300 K is 0.47 ohm-m. The electron mobility (μ_e) at 300K in Germanium is 0.39 m^2/vs. The Hole mobility μ_h =0.19 m^2/vs. Calculate density of e's in the intrinsic material. Also calculate the drift velocity of holes & e's for an electric field E = 10^4 v/m.

Soln. We have $\rho_i = 0.47\Omega m \quad \Rightarrow \quad \sigma_i = \frac{1}{\rho_i} = \frac{1}{0.47} = 2.12766.$

Density of e's $= n_i = \dfrac{\sigma_i}{e(\mu_n + \mu_p)} = 2.293 \times 10^{19} / m^3$

Drift velocity of e's $V_n = \mu_n E = 3900$ m/sec.

Drift velocity holes $V_n = \mu_p E = 1.900$ m/sec.

Example: Find the conductivity of Intrinsic Ge at 300° K. If donor type impurity is added to the extent of 1 impurity atom in 10^7 Ge atom, find the conductivity.

Given $\mathbf{n_i (300°K) = 2.5 \times 10^{13} / cm^3, \mu_n = 3800\ cm^2/vs,\ \mu_n = 1800\ cm/vs}$

Soln. $\sigma_i = n_i e(\mu_n + \mu_p) = 0.0224$ siemenper metre

Number of Ge atoms/$cm^3 = 4.41 \times 10^{22}$.
Donor Impurity = 1 donor atom/10^7 Ge atom.
Concentration of Donor atom $= N_D = 4.41 \times 10^{22}$
Concentration of e's $n = N_D = 4.41 \times 10^{15}$

Concentration of holes $p = \dfrac{n_i^2}{N_D} = \dfrac{(2.5 \times 10^{13})^2}{4.41 \times 10^{15}} = 1.417 \times 10^{11}$ hole/c

So conductivity of N-type Ge semiconductor $\sigma_n = eN_D\mu_n = 2.68$

Example: A P.D of 10 v is applied longitudinally to a rectangular specimen of intrinsic Ge of length 25 mm, width 4 mm and thickness 1.5 mm. Determine at room temp.
(i) electron and hole drift velocities.
(ii) conductivity of intrinsic Ge. If intrinsic carrier density is $2.5 \times 10^{19}/m^2$
(iii) total current.

Soln. Applied voltage V = 10 V

Length of specimen $E = \dfrac{V}{l} = \dfrac{10}{0.025} = 400$v/m

e^- drift velocity $v_n = \mu_n \times E = 0.38 \times 400 = 152$ m/sec

Hole drift velocity $v_n = \mu_p \times E = 0.18 \times 400 = 72$ m/sec

Intrinsic carrier concentration
$n_i = 2.5 \times 10^{19}/m^2$

(ii) Intrinsic conduction $= \sigma_i = n_i e(\mu_n + \mu_p) = 2.24$ si/m

(iii) Total current $I = \sigma_i Ea = 2.24 \times 400 \times 4 \times 10^{-3} \times 1.5 \times 10^{-3} = 5.376$ mA.

Example: Find the problem of occupancy of a staff of energy
(a) 6.05 eV above fermi energy
(b) 0.05 eV below fermi energy

Soln. At T = 300 K, $E_F = K_B T_F = 1.38 \times 10^{-23} \times 300\,J = 414 \times 10^{-23}\,J = 0.025$ eV.

$$f(E) = \frac{1}{\left(e^{E - E_F / K_B T} + 1\right)} = \frac{1}{\left(e^{(0.05 - 0.025)0.025} + 1\right)} = 0.119 = 12\%.$$

$$f(E) = \frac{1}{\left(e^{(-0.05 - 0.025)\ 0.025} + 1\right)} = \frac{1}{1.367} = 0.7315 = 73.15\%$$

Chapter-5: THERMAL PROPERTIES OF MATERIALS

The Specific Heat of Solid:

From elementary knowledge, we know that the specific heat is the amount of heat energy that must be supplied to a mole of solid to raise its temperature by one degree. So, when some heat energy is supplied to a solid, its temperature rises and its internal energy is increased. The increase in the internal energy is increasd. The increase in the internal energy is manifested mainly as (i) an increase in the vibration of atoms about their mean position and (ii) an increase in the kinetic energy of free electrons. The corresponding specific heats are known as the lattice specific heat and the electronic specific heat, respectively. In order to measure the specific heat and the electronic specific heat, either the volume or the pressure must be kept constant. In general, it is measured at constant volume, ie.

$$C_v = \left(\frac{dE}{dT}\right)_v \qquad \ldots (1)$$

where E is the internal energy and T is the temperature of the system.

The Classical Model:

From the kinetic theory of gases, we know that the kinetic energy of an atom of a monoatomic gas at temperature T is (3/2) kT, where 'k' is the Boltzmann constant. Since an atom has three degrees of (translational) freedom, therefore, the energy (1/2) kT, is asssociated with each degree of freedom of the atom. Also, to each translational degree of freedom, there are associated two additional degrees of freedom, because energy can appear as kinetic or potential. If there are N atoms = (N_A, Avogadro's number for a monoatomic solid) in a mole of the solid, the total internal

$$3 \times 2 \times N \times \frac{1}{2} kT = 3NkT = 3RT \qquad \ldots (2)$$

where kT = R, the universal gas constant. Therefore, the specific heat at constant volume is

$$C_v = \left(\frac{dE}{dT}\right)_v = 3R = 5.96\ cal.\ mol^{-1}K^{-1} \quad \therefore$$

This is known as Dulong and Petit's law and is found to be generally correct at room temperature and above, for elements of atomic weight greater than 40. However, the following experimental facts suggest that the above law fails under other conditions, viz,

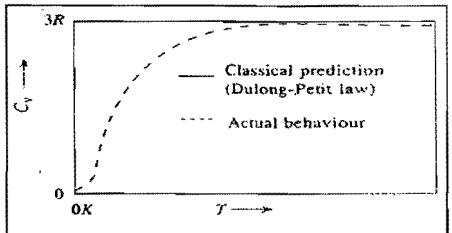


Figure: Specific heat of a solid at low temperature

1. At low temperatures, the specific heat of all elemental solids is found to appraoch zero(Figure) as T_3 in insulators and as T in metal. In superconductors, the drop is even faster.
2. In magnetic solids, there is a large contribution to the specific heat near the temperature at which the manetic moments become ordered.
3. A number of low atomic number and high melting point elements (e.g. B, Be, C and Si) show lower specific heats than predicted by Dulong petit's law.
4. A number of electropositive metals (e.g. Na, Cs, Ca and Mg) show an increase of specific heat above the

maximum value 3R with an increase of tempeature.

The Einstein Model:

Einstein was the first person to resolve the problem of specific heat of solids by the application of Planck's quantum theory. He assumed that a crystalline solid made up of N atoms (per mole) could be regarded as an array of atomic oscillators vibrating in three independent directions (as assumed for the classical calculations) with a constant frequency 'v' and that the alllowed energy states of oscillators are integral multiples by hv.

It may be shown that a crystal containing N atoms which interact according to Hooke's law is mechanically equivalent to a set of 3N independent oscillators. Thus, the total internal energy of the crystal is equal to the sum of the mean energies of the individual oscillators. Accordingly, each of the 3N harmonic oscillators will have quantised energies.

$$\varepsilon_n = n\hbar\omega = nh\nu \qquad \ldots(4)$$

when the quantum number n = 0, 1, 2, 3, ..., $\hbar = h/2\pi$ and $\omega = 2\pi\nu$. Here the 'zero point energy' (hv)/2 is neglected as it will not affect the result.

The number of oscillators N_n of each energy state is determined from the Boltzmann function as

$$N_n = N_0 \exp\left(-\frac{\varepsilon_n}{kT}\right) = N_0 \exp\left(-\frac{nh\nu}{kT}\right) \qquad \ldots(5)$$

where N_0 is the number of oscillators in the zero energy state. Further, the average vibrational energy of an oscillator is given by

$$\bar{\varepsilon} = \frac{\varepsilon}{N} = \frac{\sum_n N_n \omega_n}{\sum_n N_n} = \frac{h\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} \qquad \ldots(6)$$

Taking into the account the three independent harmonic oscillators (N and atoms and 3 independent directions), the total internal energy is given by

$$E_{mol} = \frac{3Nh\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} \qquad \ldots(7)$$

and the specific heat

$$C_v = \left(\frac{dE}{dt}\right)_v = 3Nk\left(\frac{h\nu}{kT}\right)^2 \cdot \frac{\exp\left(\frac{h\nu}{kT}\right)}{\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^2} \qquad \ldots(8)$$

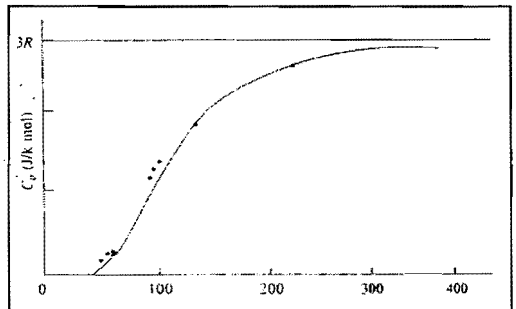


Figure: Einstein specific heat curve

The Einstein specific heat curve is fairly close to the experimental curve except at low temperature (Figure). In this region, the Einstein specific heat approaches zero more rapidly than the observed values. However, at high temperatures, it approaches the classical value. Let us consider the two temperature ranges separately.

High Temperature Range:

Let us define a quantity $x = h\nu / kT$. In this temperature range, hv << kT and therefore, the equation (6) can be written as

$$\bar{\varepsilon} = \frac{h\nu}{e^x - 1}$$

where, $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots\ldots \cong 1 + x$. Hence, at high temperature.

$$\bar{\varepsilon} = \frac{h\nu}{x} = \frac{h\nu}{h\nu} kT = kT$$

So, that $E_{mol} = 3N\bar{\varepsilon} = 3NkT$ and $C_v = \left(\frac{dE}{dT}\right)_v = 3Nk = 3R$

This is same as the classical result.

Low temperature range:

At low temperatures, hv >> kT and hence $e_x >> 1$. Therefore,

$$\bar{\varepsilon} = \frac{h\nu}{\exp\left(\frac{h\nu}{kT}\right)}$$

So, that $E_{mol} = 3N\bar{\varepsilon} = 3Nh\nu \exp\left(-\frac{h\nu}{kT}\right)$ and $C_v = \left(\frac{dE}{dT}\right)_v = 3Nh\nu\left[-\exp\left(-\frac{h\nu}{kT}\right).\frac{h\nu}{kT^2}\right]$

$$= 3Nk\left(\frac{h\nu}{kT}\right)^2 \exp\left(-\frac{h\nu}{kT}\right) \qquad \ldots (9)$$

Equation (9) indicates that the exponential term is more imporatant than the term $(h\nu / kT)^2$ in determining the variation of C_v with temperature. Thus with decreasing temperature, C_v drops exponentially.

Example: While silver metal obeys the Dulong-Petit law at room temperature, the diamond does not, explain.

Soln. According to the Einstein's theory of specific heat, if $h\nu << kT$, $C_v \to 3R$. For silver, $\nu = 4g0^{12}$ cycles/sec., so that

$$h\nu = 6626 \times 10^{-34} \times 4 \times 10^{12} = 2.65 \times 10^{-21}\ J$$

For diamond, $\nu = 2.4 \times 10^{13}$ cycles/sec, so that

$$h\nu = 6.626 \times 10^{-34} \times 2.4 \times 10^{13} = 15.9 \times 10^{-21}\ J$$

Now, at room temperature, the vlaue of kT is found to be

$$kT = 1.38 \times 10^{-23} \times 300 = 4.14 \times 10^{-21}\ J$$

Comparing these values, we find that for silver the energy hv is less than kT while for the diamond it is high. The high value of energy (or frequency) is due to strong covalent bonding between the adjacent carbon atoms. As a result, much higher temeprature is required for the Dulong-Petit law to obeyed in this case.

The density of states:

One of the important problems of the theory of lattice vibrations is to find out the frequency distribution of normal modes. For the purpose we consider a one-dimensional chain of atoms (string) of length L with fixed ends (Figure) and that only longitudinal displacement occurs in it. Suppose u(x, t) represents the displacement of string at any point 'x' at a time 't'. The one dimensional wave equation describing the displacement is:

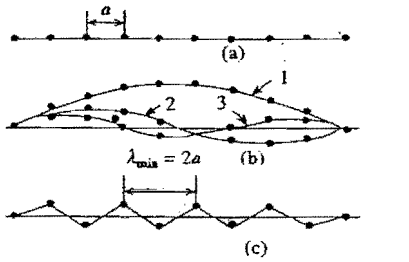


Figure: Normal modes of a linear chain of identical atoms (a) linear chain (b) normal modes of the chain (c) normal modes of the chain corresponding to shortest wavelength(to highest frequency)

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 u}{\partial t^2} \qquad \ldots (10)$$

where 'v' is the velocity of the wave in the string. Solving for above boundary conditions (i.e. u = 0 at x = 0 and x = L), the normal mode solutions of equation (10) are obtained in the form of standing waves as

$$u(x,t) = A\sin\left(\frac{n\pi x}{L}\right)\cos 2\pi\nu_n t \qquad \ldots (11)$$

where 'n' is any positive integer ≥ 1 and A is a constant. In such cases, there should be an integral number of half wavelength in the chain, i.e.

$$L = n\frac{\lambda}{2}$$

Differentiating equation (11) with respect to x and t twice, we get

$$\frac{\partial^2 u}{\partial x^2} = -\frac{un^2\pi^2}{L^2} \text{ and } \frac{\partial^2 u}{\partial t^2} = -u4\pi^2\nu^2 \qquad \ldots (12)$$

Substituting these values in equation (10), the frequency can be obtained as

$$\nu^2 = \frac{n^2 v^2}{4L^2} \qquad \ldots (13)$$

The wavelength and frequencies of the possible vibrations represented by equation (11), are given by

$$\lambda_n = \frac{2L}{n} \text{ and } \nu_n = \frac{v}{\lambda_n} = n\left(\frac{v}{2L}\right) \qquad \ldots (14)$$

The frequency spectrum is discrete, one frequency corresponds to each integer value n. Therefore, the number of possible modes of vibrations g(ν) in a frequency interval dν is, on the average

$$g(\nu) = dn = \frac{2L}{v}d\nu \qquad \ldots (15)$$

According to equation (15), the frequency spectrum corresponds to an infinite number of equidistant lines, as shown in figure (below).

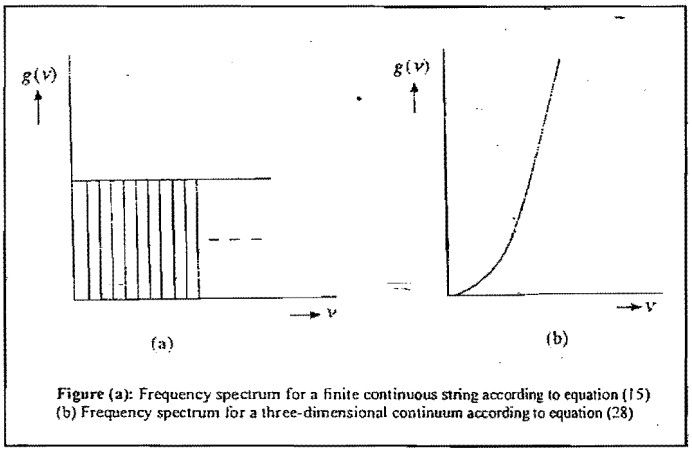


Figure (a): Frequency spectrum for a finite continuous string according to equation (15)
(b) Frequency spectrum for a three-dimensional continuum according to equation (28)

In a three dimensional case, the situation is different. In this case, we have two distinguishable velocities of propagation, v_l for longitudinal wave (a non-degenerate mode) along the direction of propagation and v_t for the transverse wave (doubly degenerate modes) perpendicular to the direction of propagation. Consequently, we have two different equations involving v_l and v_t, each analogous to equation (10), i.e.,

$$\frac{\partial^2 u_l}{\partial x^2}+\frac{\partial^2 u_l}{\partial y^2}+\frac{\partial^2 u_l}{\partial z^2}=\frac{1}{v_l^2}\frac{\partial^2 u_l}{\partial t^2} \qquad \ldots(16)$$

And

$$\frac{\partial^2 u_t}{\partial x^2}+\frac{\partial^2 u_t}{\partial y^2}+\frac{\partial^2 u_t}{\partial z^2}=\frac{1}{v_t^2}\frac{\partial^2 u_t}{\partial t^2} \qquad \ldots(17)$$

Choosing again the simplest boundary conditions that the surface planes of the cube are rigidly held, we obtain the following standing wave solutions.

$$u_l(x,y,z)=A_l\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{\pi_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right)\cos 2\pi\nu_l t \qquad \ldots(18)$$

and

$$u_t(x,y,z)=A_t\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{\pi_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right)\cos 2\pi\nu_t t \qquad \ldots(19)$$

where n_x, n_y and n_z are positive integers ≥ 1 and A_l and A_t are constants as pointed out earlier.
Differentiating equation (18) and (19) with respect to x, y, z, twice and substituting the resulting values in equation (16) and (17), we obtain the following expressions for the possible modes of vibration,

$$\nu_l^2=\frac{v_l^2}{4L^2}\left(n_x^2+n_y^2+n_z^2\right) \qquad \ldots(20)$$

and

$$\nu_t^2=\frac{v_t^2}{4L^2}\left(n_x^2+n_y^2+n_z^2\right) \qquad \ldots(21)$$

Thus, for any chosen set of integers, n_x, n_y and n_z, there are three independent modes of the vibrations (one longitudinal and two values). Now, employing the relation, $k=\frac{\pi}{\lambda}=\frac{2\pi\nu}{v}$, the components of the wave vector 'k' from equation (20) can be written as

$$k_x=\frac{\pi n_x}{L},\ k_y=\frac{\pi n_y}{L},\ k_z=\frac{\pi n_z}{L} \qquad \ldots(22)$$

Further, if we suppose that $k^2 = k_x^2 + k_y^2 + k_z^2$, then from equation (20) and (21), it follows that

$$v_l = \frac{v_l k}{2\pi} \text{ and } v_t = \frac{v_t k}{2\pi} \quad \ldots (23)$$

Where 'k' may now be identified as the wave vector with the components k_x, k_y and k_z are 'r' as the position vector. A plot of allowed values of 'k' in reciprocal space or k-space is shown in figure below. Points defined in equation (22) are distributed as lattice points in the positive octant. The volume of the octant of radius 'k' is

$$\frac{1}{8} \times \frac{4}{3} \pi k^3 = \frac{1}{6} \pi k^3$$

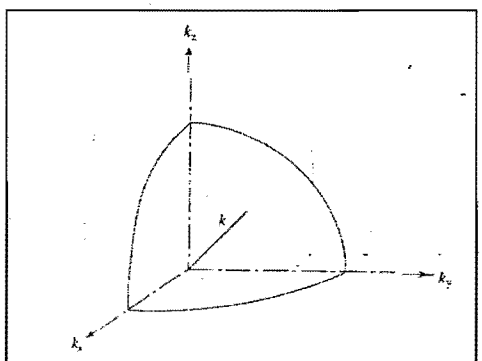


Figure: Representation of wave vectors in k-space

and the volume occupied by each point is $(\pi/L)^3$. Therefore, the total number of lattice points in the octant is

$$\frac{Vk^3}{6\pi^2}$$

where V (= L^3) is the volume of the crystal. For a particular frequency v, the equation (23) will give rise to two wave numbers k_l and k_t as

$$k_l = \frac{2\pi v}{v_l} \text{ and } k_t = \frac{2\pi v}{v_t} \quad \ldots (24)$$

Thus, the total number of lattice points in the octant with the radii k_l and k_t, respectively are

$$\frac{V}{6\pi^2}\left(\frac{2\pi v}{v_l}\right) \text{ and } \frac{V}{6\pi^2}\left(\frac{2\pi v}{v_t}\right)^3$$

However, since with every lattice point, we may associate one longitudinal mode and two tranverse modes, the number of modes g(v) of frequency less than v_D is given by

$$g(v) = \frac{8\pi^3 V}{6\pi^2}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)v^3 \quad \ldots (25)$$

where a mean velocity 'v' may be defined by the equation

$$\frac{3}{v^3} = \frac{1}{v_l^3} + \frac{2}{v_t^3} \quad \ldots (26)$$

So, that equation (25) becomes, $g(v) = \frac{4\pi V v^3}{v^3}$ ... (27)

Differentiating this expression, we obtain the required frequency distribution fnction

$$g(\nu)\,d\nu = \frac{12\pi V}{\nu^3}\nu^2 d\nu \qquad \ldots(28)$$

or similarly from equation (25), we obtain,

$$g(\nu)\,d\nu = 4\pi V\left(\frac{1}{\nu_l^3}+\frac{2}{\nu_t^3}\right)\nu^2 d\nu \qquad \ldots(29)$$

This is the number of modes whose frequencies lie between the interval v and v + dv. A curve between the density of states g(v) and v(figure) shows that g(v) increases as v^2. The function g(v) is also known as spectral distribution function of normal modes.

Since the number of normal vibrations in a three dimensional crystal lattice is 3N, the function g(v) should satisfy the following normalization condition.

$$\int_0^{\nu_D} g(\nu)\,d\nu = 3N \qquad \ldots(30)$$

where 'ν_D' is the maximum frequency limiting the spectrum of normal modes from above and is known as Debye frequency. Substituting equation (29) into equation(30) and integrating, we obtain

$$4\pi V\left(\frac{1}{\nu_l^3}+\frac{2}{\nu_t^3}\right)\int_0^{\nu_D}\nu^2 d\nu = 3N$$

$$\Rightarrow \qquad \nu_D^3 = \frac{9N}{4\pi V}\left(\frac{1}{\nu_l^3}+\frac{2}{\nu_t^3}\right)^{-1} \qquad \ldots(31)$$

Substituting equation (31) back into equation (29), we obtain the distribution function

$$f(\nu) = \sum_{l,t} g(\nu) = \frac{9N}{\nu_D^3}\nu^2$$

which gives, $f(\nu) = K\nu^2 \quad (\text{for } \nu \le \nu_D)$ ...(32)

$= 0 \quad (\text{for } \nu \le \nu_D)$

where $K = \dfrac{9N}{\nu_D^3}$ is a constant (independent of v). This function is compared with the Einstein's function in figure ( ).

The Debye Model:

In 1912, Debye pointed out that the source of error lies in the assumption (that all atomic oscillators vibrate independently at a constant frequency) made by Einstein. According to him, the assumption is not justifiable since all atoms are elastically coupled to its neighbours, as shown in figure ( ). Debye therefore, simplified the problem by considering a solid as a continuously vibrating medium (as an elastic continuum), which gives rise to a spectrum of frequencies instead of a single frequency as assumed in the Einstein's model. Once, the frequency distribution is known, it is a simple matter to calculate the total internal energy and the hence the specific heat of the solids. Taking into account the density of states as obtained in the preceding section, we can write the internal energy of the Debye solid as

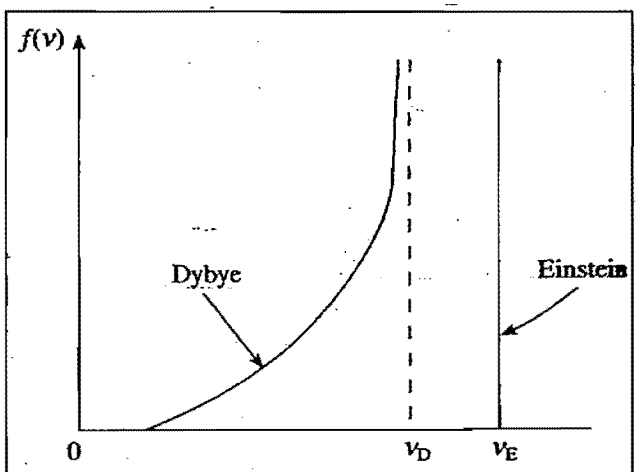


Figure: Frequency spectrum according to Debye model and Einstein model

$$E = \int_{\substack{\text{all allowed} \\ \text{frequencies}}} \bar{\varepsilon}(\nu) g(\nu) d\nu \qquad \ldots (33)$$

Using equation (6) and (29), we get

$$E = 4\pi V \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \int_0^{\nu_D} \frac{h\nu\nu^2 d\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1}$$

which in terms of equation (31) can be written as

$$E = \frac{9N}{\nu_D^3} \int_0^{\nu_D} \frac{h\nu\nu^2 d\nu}{\exp\left(\frac{h\nu}{kT}\right) - 1} \qquad \ldots (34)$$

To simplify equation (34), let us suppose that $x = h\nu / kT$, so that $d\nu = (kT\, dx)/h$. Further, if we suppose that $x_D = (h\nu_D)/kT$, equation (34) becomes

$$E = 9N \left(\frac{kT}{h\nu_D} \right)^3 kT \int_0^{x_D} \frac{x^3}{e^x - 1} dx \qquad \ldots (35)$$

Now, we can define the Debye temperature as θ_D according to the equation, $h\nu_D = k\theta_D$, then

$$\theta_D = \frac{h\nu_D}{k} \text{ and } x_D = \frac{\theta_D}{T}$$

So, that equation (35) becomes

$$E = 9NkT \left(\frac{T}{\theta_D} \right)^3 \int_0^{\nu_D} \frac{x^3}{e^x - 1} dx \qquad \ldots (36)$$

which does not depend explicitly on the volume and looks similar to the expression obtained for Einstein's model. However, let us examine the dependence of the integral (equation 36) on temperature. For simplicity,

we shall consider the following three temperature ranges.

High Temperature Range:

We assumed earlier that $x = h\nu / kT$. In this temperature range, $T >> \theta_D$ and hence kT >> h_ν even when ν = ν_D, implying that 'x' will be small over the whole range of the integration. So, that

$$\int_0^{x_D} \frac{x^3}{e^x - 1} dx \to \int_0^{x_D} \frac{x^3}{x} dx = \frac{x_D^3}{3} = \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

Therefore, $$E = 9NkT \times \frac{1}{3} = 3NkT \qquad \ldots (37)$$

which is the classical result. This implies that in the high temperature range, the specific heat of solids is the same as measured in Dulong and Petit's experiment. This can be undesrstood from the following arguments: when $T >> \theta_D$, every mode of oscillation is completely excited, and has an average energy equal to the classical value i.e. $\bar{\varepsilon} = kT$. Substituting this in equation (33) and also making use of the equation (30), we obtain, $E = 3NkT$, which is sameas equation (37).

Low temperature range:

In the low temperature range, $T << \theta_D$, so that $kT << h\nu_D$. In this case, the upper limit of the integration can be replaced by infinity (i.e. $x_D \to \infty$) and hence the above integral becomes

$$\int_0^{x_D} \frac{x^3}{e^x - 1} dx \to \int_0^{\infty} \frac{x^3}{e^x - 1} dx \to \frac{\pi^4}{15}$$

Therefore, $$E = 9NkT\left(\frac{T}{\theta_D}\right)^3 \times \frac{\pi^4}{15} = \frac{3}{5}\pi^4 NkT\left(\frac{T}{\theta_D}\right)^3$$

and $$C_\nu = \frac{12}{5}\pi^4 Nk\left(\frac{T}{\theta_D}\right)^3 \qquad \ldots (38)$$

This is a famous expression known as Debye T^3 law for specific heat at low temperature. Figure ( ) shows a typical Debye plot alongwith the measured data, Einstein plot and the classical value.

Example: (i) Calculate Eisteins frequency for copper for which $\theta_E = 230k$. Given $h = 6.6 \times 10^{-34}$ J-sec. Boltzmann constant $k = 1.37 \times 10^{-23}$ Joule/k.

(ii) Use result (i) to show that the classical result $C_V = 3R$ should be valid for copper if T > 230°C

Soln **(i)** Einsteins's frequency ν_E is given by

$$\frac{h\nu_E}{K} = \theta_E$$

Where h is plank's constant and k is Boltzmann's constant

$h = 6.6 \times 10^{-34}$ J/sec, $k = 1.37 \times 10^{-23}$ J/k, $\theta_E = 230$ k

$$\therefore \nu_E = \frac{\theta_E k}{h} = \frac{230 \times 1.37 \times 10^{-23}}{6.6 \times 10^{-34}} = 4.794 \times 10^{12}\ \text{sec}^{-1}$$

(ii) $C_V = 3R$ If $T >> \frac{h\nu}{k}$

$$\therefore \frac{h\nu}{k} = \frac{6.6\times10^{-34}\times4.794\times10^{12}}{1.37\times10^{-23}} = 230k$$

Example: Calculate Einstein's frequency for a case for which $\theta_E = 236k$ Given $k = 1.4\times10^{-23}$ Joule/K, $h = 6.6\times10^{-34}$ J/sec

Soln. $\nu_E = \frac{\theta_E k}{h} = \frac{237\times1.4\times10^{-23}}{6.6\times10^{-34}} = 5\times10^{12}\ sec^{-1}$

Example: (a) For copper $\nu = 2.49\times10^{12}$ cycle/sec (Hertz) Calculate the characteristic temperature θ_E.

(b) For copper the value C_V is 23.8 Joule/mole k while for Diamond the value of C_V is only 6.1 Joule/mole k (both values are at T = 300 k). How do you account for this difference?

Given $h = 6.6\times10^{-34}$ Joule/sec, $k = 1.38\times10^{-23}$ Joule/k

Soln. (a) The characteristic temperature

$$\theta_E = \frac{h\nu}{k} \qquad \therefore \theta_E = \frac{6.6\times10^{-34}\times2.49\times10^{12}}{1.38\times10^{-23}} = 119.1\,k$$

(b) According to Einstein theory, the specific that of solid.

$$C_v = 3R\left[\frac{e^{\theta/T}}{\left(e^{\theta/T}-1\right)^2}(\theta/T)^2\right]$$

Where $\theta = \frac{h\nu}{k}$ is called Einsteins temp and ν is Eisteins's frequency.

for same temp T, the values of C_v for copper and diamond differ only due to their different values of ν

Example: For Copper At. Wt. = 63.5, density 8.95 gm.c and Compressibility $\beta = 7.3\times10^{-13}\ cm^2/dyne^{-1}$

Using these data universal constant N, k and h deduce the following:

(i) mass m of copper atom.

(ii) the interatomic distance a assuming simple cubic Lattice

(iii) frequency of vibration $\nu = \frac{1}{2\pi}\sqrt{\frac{3a}{\beta m}}$

(iv) use result (iii) to show that classical theory result $C_v = 3R$ should be valid for copper if $T << 230$ k.

Soln. (i) Mass of copper atom $m = \frac{At.wt}{Avogadro\ no.}$

$$= \frac{63.5}{6.02\times10^{23}} = 1.05\times10^{-22}\,gm$$

(ii) Interatomic distance $a = \left(\frac{nA}{N\rho}\right)^{1/3}$

here n = lattice points per unit cell = 1 for sc lattice.

A = At. Wt. = 63.5

N = Avogadro No. = 6.02×10^{23}

ρ = density of copper = 8.95 gm.cm^{-3}

N = Avogadro No. $= 6.02 \times 10^{23}$

ρ = density of copper $= 8.95\ gm.cm^{-3}$

$$\therefore a = \left(\frac{1 \times 63.5}{6.02 \times 10^{23} \times 8.95}\right)^{1/3}$$

$$\log a = \frac{1}{3}[\log 63.5 - \log 6.02 - 23 - \log 8.95] = \frac{1}{3}[1.8028 - 0.7796 - 23 - 0.9513] = 8.3572$$

$$a = 2.281 \times 10^{-8}\ cm = 2.281\ \text{Å}$$

(iii) $$\nu = \frac{1}{2\pi}\sqrt{\frac{3a}{\beta m}}$$

$$= \frac{1}{2 \times 3.14}\sqrt{\left(\frac{3 \times 2.281 \times 10^{-8}}{7.3 \times 10^{-13} \times 1.05 \times 10^{-22}}\right)}$$

$$\log \nu = -\log 2 - \log 3.14 + \frac{1}{2}[\log 3 + \log 2.281 - 8 - \log 7.3 - 13 - \log 1.05 + 22]$$

$$= 0.3010 - 0.4969 + \frac{1}{2}[0.4771 + 0.3581 - 8.9633 + 13 - 0.0212 + 22]$$

$$= 12.6774$$

$$\nu = 4.757 \times 10^{12}\ \text{cycle/sec}$$

(iv) According to Einsteins theory of atomic heat C_v approaches the value 3R if

$$\frac{h\nu}{k} << 1 \text{ i.e., if } \frac{h\nu}{k} < T \text{ i.e. If } T > \frac{h\nu}{k}$$

$$\therefore \text{Here } \frac{h\nu}{k} = \frac{\left(6.62 \times 10^{-34}\right) \times \left(4.75 \times 10^{12}\ \text{sec}^{-1}\right)}{1.38 \times 10^{-23}\ \text{Joule/K}}$$

$$= 230°K$$

$\therefore$ for copper classical theory result $C_v = 3R$ is valid of $T > 230$ K

Example: The specific heat C of a certain substance at very low temperature is found to depend on the absolute temp. T according to the relation $C = AT^3$. Where A = const.
(i) If units are calories, gram and kelvin degree what units must the constant A have?
(ii) How much heat must be added to raise the temperatures of a mass m of the material from T_1 to T_2?

Soln. (i) Given $C = AT^3$ $\quad\quad \therefore A = C/T^3$

unit of sp. heat is cal. per gm per kelvin and that T is kelvin
so unit of A. is

$$\frac{\text{cal per gm per kelvin}}{(\text{kelvin})^3} = \text{cal per gm per } (\text{kelvin})^4$$

or $\quad\quad \text{Cal gm}^{-1}\,(k)^{-4}$

(ii) Heat required to raise the temperature of mass m of the material by dT, = mcdT. So heat required to raise the temperature of a mass m of the material from T_1 to T_2

$$= \int_{T_1}^{T_2} mcdT = \int_{T_1}^{T_2} mAT^3 dT = mA\left[\frac{T^4}{4}\right]_{T_1}^{T_2} = \frac{1}{4}mA\left(T_2^4 - T_1^4\right)$$

Example: The Debye temperature of carbon (Diamond) is 1850 k. Calculate the sp. heat per kmol. for diamond at 20 k. Also compute the highest lattice frequency involved in the Debye theory.

Soln. Specific heat at low temperature

$$C_v = 3R \times 12\left(\frac{T}{\theta}\right)^3 \frac{\pi^4}{15} = 77.94 \times 3R\left(\frac{T}{\theta}\right)^3 = 77.94 \times 3R\left(\frac{20}{1850}\right)^3$$

Lattice frequency $\nu_m = k\frac{\theta}{h}$ where $\theta = 1850$ k

Example: Calculate the Debye specific heat of copper at (i) 10 k and (ii) 300 k , given that the Debye characteristic frequency is 6.55×10^{12} Hz.

Soln. $\nu_m = k\theta/h \quad \therefore \theta = \frac{\nu_m h}{k} \quad \therefore$ Specific heat $C_V = 77.94 \times 3R\left(\frac{T}{\theta}\right)^3$

Example: In Aluminium, $v_l = 6.32 \times 10^3 m/sec$ and $V_t = 3.1 \times 10^3 m/sec$. The density of Aluminium is 2.7×10^3 kg/m^3 and its atomic wt. is 26.97.

(a) Calculate the Debye cut off frequency (ν_D) for Aluminium for these data.

(b)The Debye temperature for Aluminium as obtained from specific heat measurements is 375 k. Find ν_D from this figure and compare it with results obtained in (a)

(c)Are the preceding values of ν_D consistent with the vibtrational frequency of Aluminium atoms in solid Aluminium?

Hints: $4\pi V\left[\frac{1}{C_l^3} + \frac{2}{C_t^3}\right] = \frac{9N}{\nu_m^3}$

$$\text{density} = \frac{\text{mass}}{\text{Volume}} \Rightarrow \text{Volume} = \frac{\text{Mass}}{\text{Density}}$$

$\Rightarrow$ V = Volume of gm-molecule of Solid.

(ii) $\theta = 375$ k. $\quad \nu_m = k\frac{\theta}{h}$

Example: For copper, the lattice specific heat at low temperature has the behaviors of $C_V = 4.6 \times 10^{-2} T^3 J/mol-k$. Estimate the Debye temp. of Copper

Hints: $C_V = 77.94 \times 3R\left(\frac{T}{\theta}\right)^3$

Example: At very low temperatures, the specific heat of Rock salt varies with temperature according to Debye T^3 low

$$[C_v]_{la} = \frac{12\pi^4 N_A k_B}{5}\left[\frac{T}{\theta_D}\right]^3$$

θ_D for Rock salt is 281 k. How much heat is required to raise the temperature of 2 k mol of Rock salt from 10 to 50 k.

Hints: Heat = mcdT $= \int_{T_1}^{T_2} m\left(\frac{12\pi^4 N_A k_B}{5}\right)\left[\frac{T}{\theta_D}\right]^3 dT$

$$= m\left[\frac{12\pi^4 N_A k_B}{5}\right]\left(\frac{1}{\theta_D^3}\right)\int_{T_1}^{T_2} T^3 dT$$

Example: Copper has an atomic wt. 63.5, a density of 8.9×10^3 kg/m^3 and $V_t = 2.32 \times 10^3$ m/sec and $V_\ell = 4.76 \times 10^3 m/sec$. Estimate the specific heat at low temp. say at 30 k.

Hints: $v_D^3 = \frac{9N}{4\pi V}\left[\frac{2}{V_t^3} + \frac{1}{V_\ell^3}\right]^{-1}$

$v_D = \frac{k\theta}{h}$ get θ,

then C_V at low temp. $C_V = 77.94 \times 3R\left(\frac{T}{\theta}\right)^3$ where T = 30 K.

Chapter-6: TRANSPORT PHENOMENA

Thermal conductivity of Solids:

Thermal conductivity is a process in which heat is transferred from one part of the body to the another as a result of temperature gradient. If the gradient is uniform, then the amount of the thermal energy crossing a unit area in unit time is directly proportional to the temperature gradient, i.e.

$$Q \propto \frac{dT}{dx} \qquad \Rightarrow Q = K\left(\frac{dT}{dx}\right) \qquad \ldots (1)$$

where the proportionality constant K is called the thermal conductivity. In metallic conductors, heat is carried by free electrons, while in insulators, it is mainly carried by phonons. Therefore, in general the transfer of heat can take place both by electrons and phonons and hence the total thermal conductivity can be written as

$$K_{total} = K_{electron} + K_{phonon} \qquad \ldots (2)$$

In order to determine the value of K in equation (40), let us consider a conductor in the form of rod of uniform cross-section (say 1 sq.m) with the assumption that there exists a uniform temperature gradient. Let us draw three parallel planes at A, B and C normal to the direction of heat flow which are separated by one mean free path λ as shown in figure below.

According to the kinetic theory, the number of electrons flowing in a given direction through unit area in unit time is $\frac{1}{6}(nv)$, where 'n' is the density of electrons moving with an average velocity v. Further, the excess of energy flowing through the plane B to the right is:

$$Q_{right} = \frac{1}{6} nv\lambda \left(\frac{dE}{dx}\right) \qquad \ldots (3)$$

Similarly, the energy flowing through the plane B to the left is

$$Q_{left} = -\frac{1}{6} nv\lambda \left(\frac{dE}{dx}\right) \qquad \ldots (4)$$

Therefore, the net amount of energy flowing through the plane B is

$$Q = Q_{right} - Q_{left} = \frac{1}{6} nv\lambda \left(\frac{dE}{dx}\right) - \left[-\frac{1}{6} nv\lambda \left(\frac{dE}{dx}\right)\right] = \frac{nv\lambda}{3}\left(\frac{dE}{dx}\right) \qquad \ldots (5)$$

But $$n\left(\frac{dE}{dx}\right) = n\left(\frac{dE}{dT}\right)\left(\frac{dT}{dx}\right) = nC_v\left(\frac{dT}{dx}\right)$$

where Cv is the specific heat of solid at constant volume. Therefore, equation (5) becomes

$$Q = \frac{nC_v v\lambda}{3}\left(\frac{dT}{dx}\right) \qquad \ldots (6)$$

Now, comparing equations (1) and (6), we obtain

$$K = \frac{1}{3} v\lambda C_v \qquad \ldots (7)$$

Thermal conductivity due to electrons:

In order to derive an expression for thermal conductivity of metals where the heat is predominantly carried by the electrons, we make the following assumptions:

(i) The metal consists of fixed positive ions in a sea of electrons. In general, there will be one or two electrons per ion.

(ii) The electrons behave as a perfect gas and they transport thermal energy from the hotter to the colder region.

(iii) Each electron travels a distance λ in a mean free time τ before colliding with a positive ion where it gives up all its thermal energy.

(iv) Only those electrons that lie within the range kT of the Fermi level are active in the transport process. The velocity of such electrons is calculated from the formula.

$$\frac{1}{2}mv_F^2 = E_F \qquad \ldots(8)$$

Substituting the value of electronic specific heat from equation (5) and $\lambda = v_F\tau$ in equation (7) and making use of equation (8), we obtain the electronic contribution of thermal conductivity as

$$K_e = \left(\frac{3\tau E_F}{3m}\right)\left(\frac{\pi^2 Nk^2}{2E_F}\right)T = \left(\frac{\pi^2 Nk^2\tau}{3m}\right)T \qquad \ldots(9)$$

Since, the mean free time τ varies as T^{-1} above the Debye temperature, the electronic contribution of thermal conductivity is nearly temperature independent. This is consistent with the experimental facts.

Thermal conductivity due to phonons:

As we know that in insulators, there are no mobile electrons and hence phonons carry most of the heat energy. Thus, for insulators in equation (7), v is the velocity of sound, λ is the phonon mean free path and C_v is the lattice specific heat per unit volume given by the Debye T^3 law:

$$C_v = \begin{cases} \alpha T^3 & (T < \theta_D) \\ 3nK & (T > \theta_D) \end{cases} \qquad \ldots(50)$$

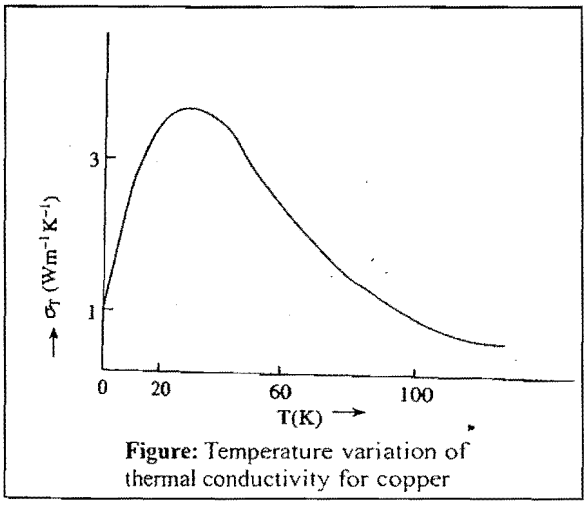


Figure: Temperature variation of thermal conductivity for copper

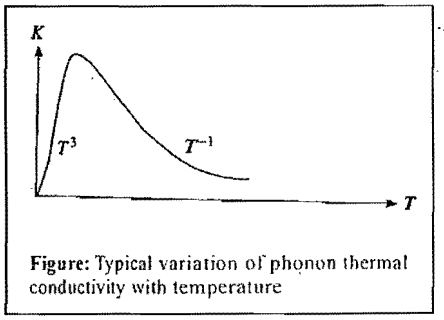


Figure: Typical variation of phonon thermal conductivity with temperature

Consequently, the thermal conductivity of an insulator is proportional to T^3 at low temperatures, as shown in figure . At high temperatures $(T >> \theta_D)$, the lattice specific heat is constant (i.e., equal to 3Nk, the Dulong-Petit's value) and any temperature dependence of K arises predominantly from the variation of the mean free path λ due to phonon-phonon interaction (i.e. due to anharmonicity). However, a small contribution may also arise fromm collisions of phonons with crystal boundaries and impurities. Therefore, for all practical purposes only phonon-phonon contribution is considered. The lattice dynamics of anharmonic crystals which takes into account the phonon-phonon collision is very complicated, but leads to a simple final result, viz. the phonon mean free paht is inversely proportional to the abosolute temperature, i.e. $\lambda = T^{-1}$, so that,

$$K = T^{-1} \qquad \ldots (11)$$

Thus, the thermal conductivity of an insulator is proportional to T^{-1} at high temperatures.

The Drude Theory:

The Drude model assumes that the electrons in a metal are free to move and form an 'electron gas. The basic assumptions of the Drude model are the following.

(i) The electrons are in thermal equilibrium with the environment.

(ii) Between collisions, the interactions of an electron with the other electrons and with the ions are negligible. Thus the electron travels uniformly in a straight line between collisions in the absence of applied electro-magnetic fields. The motion of electrons in the presence of applied fields is determined by Newton's laws of motion.

(iii) The time taken up in a collision is negligible. The velocity of an electron changes abruptly when it undergoes a collision.

(iv) The electron-electron collisions are usually unimportant.

(v) The metallic ions form the major source of collisions. The exact nature of the scattering is not required; only some broad features associated with the scattering are important. The probability per unit time for an electron to suffer a collision is assumed to be $1/\tau$. The time 'τ' is referred to as the relaxation time, the collision time or the mean free time. For simplicity, 'τ' is taken to be independent of the position and velocity of the electron.

Electrical Conductivity:

In the absence of an electric field, the free electrons in a metal move at random owing to their thermal energy. At each collision, the path of the electron is changed. . The number of electrons moving in one electrons moving in one direction is the same as that moving in the opposite direction, so that considering all the electrons the average drift velocity is zero. When an electric field is applied, the electrons are accelerated between collisions. As an electron carries a negative charge the acceleration is opposite to the direction of the field. Immediately after collisions, all the electron velocities are randomised. In equilibrium, all the electrons possess a common drift velocity due to the electric field . The drift velocity has a very small magnitude compared to the random thermal velocity on which it is superimposed. The electron drift gives rise to the current flow through the metal.

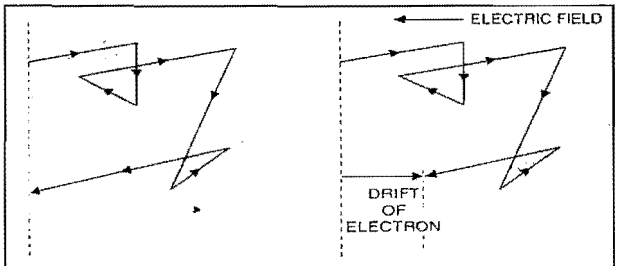


Figure: (a) Random electron motion, and (b) electron drift in an applied electric field

The electrical conductivity σ of a solid is the charge conducted per unit time across unit area of the solid for applied unit electric field. If due to an applied electric field ξ the current density, i.e. the current per unit cross sectional area is J, the conductivity σ is given by $\sigma = \frac{J}{\xi}$ ... (12)

In SI units J is expressed in A/m^2, ξ in volt/m, and σ in siemens/m.

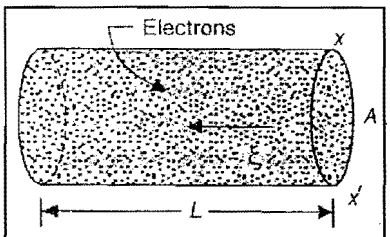


Figure: Geometry for calculation of current density

Consider a cylinderical metal of length L and having an area of cross section A (figure .....). If 'v' is the drift velocity of the electrons for an electric field ξ applied along the length of hte cylinder, the the time taken by an electron to traverse the distance L as $t = \frac{L}{v}$ ... (13)

If 'n' represents the electron concentration then the total number of electrons contained in the cylinder is nAL. The charge inside the cylinder is, therefore, nALe, where 'e' is electronic charge. This amount of charge moves through the cross section xx' in time 't'. Therefore, the current flowing through the metallic cylinder is:

$$I = \frac{nALe}{t} \quad \ldots (14)$$

The current density J will be $J = \frac{I}{A} = \frac{nLe}{t} = nev$ ... (15)

From equation (12) and (15) we get

$$\sigma = ne\frac{v}{\xi} \quad \ldots (16)$$

The quantity v/ξ, i.e. the drift velocity per unit electric field is termed the mobility of the electron. Denoting the mobility by μ we have, $\sigma = ne\mu$ ... (17)

In SI units, μ is expressed in $m^2/(V.s)$.

Mean Free Time:

As already mentioned, the probability of an electron suffering a collision in unit time is $1/\tau$. The quantity 'τ' is a constant depending on the system and has the dimension of time.

Consider a group of n_0 electrons at time t = 0. Let 'n' denote the number of electrons in the group which do not make a collision in time 't'. If dn be the change in 'n' due to collision in a further time dt, then

$$dn = -\frac{n}{\tau}dt \quad \ldots (18)$$

$$\Rightarrow n = n_0 \exp(-1/\tau) \quad \ldots (19)$$

The mean free time of an electron is given by the total lifetime of all the n_0 electrons divided by n_0. Thus,

$$\text{Mean free time} = -\frac{1}{n_0}\int_0^\infty t\, dn = \frac{1}{\tau}\int_0^\infty t \exp(-1/\tau)dt = \tau \quad ...(20)$$

Thus the quantity τ represents the mean free time of an electron between collisions. The mean free path of an electron is given by $\ell = \tau\bar{v}$

where '$\bar{v}$' represents the average velocity of the electron.

During the time between collisions an electron has an acceleration $e\xi/m_e$, where 'e' is the electron charge, ξ is the electric field, the m_e is the mass of the electron. As an electron, observed at a random instant of time, travels freely on the average for a time τ, the average drift velocity v_d of the electron will be

$$v_d = \frac{e\xi\tau}{m_e} \quad ...(21)$$

The mobility of the electron is given by $\mu = \frac{v_d}{\xi} = \frac{e\tau}{m_e}$ ...(22)

An order of magnitude of 'τ' can be obtained by noting that for copper $\mu = 3\times10^{-3}\ m^2/(V.s.)$. Substituting the values $e = 1.6\times10^{-19}$ coulomb and $m_e = 9.11\times10^{-31}$ kg, we obtain from equation (22) $\tau \approx 1.7\times10^{-14}$ s. The value is however not very accurate since the effective mass of an electron in metal is not exactly equal to the free electron mass. Also, strictly speaking, 'τ' is not a constant but depends on the electron energy.

From equation (17) and (22) we express the conductivity σ in the form:

$$\sigma = \frac{ne^2\tau}{m_e} \quad ..(23).$$

Thermal Conductivity of a Metal:

We shall now developed an expression for the thermal conductivity due to free electrons in a metal.

Assume a temperature gradient $\frac{dT}{dx}$ in the x-direction. The thermal current density Jq represents the thermal energy crossing a unit area perpendicular to the direction of flow per unit time. It is given by

$$J_q = -K\frac{dT}{dx} \quad ...(24)$$

where K is a positive constant, referred to as the thermal conductivity. The negative sign in equation (24) appears since the heat flow is opposite to the direction of temperature gradient.

After each collision an electron moves with a speed appropriate to the local temperature. Thus an electron emerging from a hotter place of collision will be more energetic. Let E(T) represent the thermal energy of an electron at temperature T. Hence an electron suffering the last collision at the position coordinate 'x' will carry on the average a thermal energy $E[T(x')]$. The electrons that come to the point 'x' from the high temperature side had their last collision at $x' = (x - v_x\tau)$ where v_x is the x-component of the average velocity of the electrons and 'τ' the mean free time. The average thermal energy associated with each such electron is $E[T(x - v_x\tau)]$. If 'n' be the total number of electrons per unit volume, half of this number will come to the point 'x' from the high-temperatue side and half from the low-temperature side. The thermal current density at x due to the electrons coming from the high-temperature side will be

$$J_{qh} = \frac{n}{2} v_x E\left[T\left(x - v_x\tau\right)\right] \qquad \ldots(25)$$

Similarly, the thermal current density due to the electrons coming to 'x' from the low temperature side is:

$$J_{q'} = \frac{n}{2}\left(-v_x\right) E\left[T\left(x + v_x\tau\right)\right] \qquad \ldots(26)$$

since these electrons move in the negative x-direction. The net thermal current at 'x' is:

$$J_q = J_{qh} + J_{q'} = \frac{nv_x}{2}\left[E\left\{T\left(x - v_x\tau\right)\right\} - E\left\{T\left(x + v_x\tau\right)\right\}\right]$$

It may be assumed that the variation of the temperature over the mean free path $= v_x\tau$ is very small. Thus expanding in a Taylor series and neglecting the higher order terms we get

$$J_q = nv_x^2\tau\frac{dE}{dT}\left(-\frac{dT}{dx}\right) \qquad \ldots(27)$$

We shall now replace v_x^2 by its average value $v^2/3$ where v^2 is the mean square velocity. Hence

$$J_q = \frac{1}{3}nv^2\tau\frac{dE}{dT}\left(-\frac{dT}{dx}\right) \qquad \ldots(28)$$

If N be the total number of free electrons and V be the volume of the metal we have

$$n\frac{dE}{dT} = \frac{N}{V}\frac{dE}{dT} = C_v \qquad \ldots(29)$$

where C_v is the electronic heat capacity per unit volume. Using equation (29) in equation (28) we obtain

$$J_q = -\frac{1}{3}v^2\tau\, C_v\frac{dT}{dx} \qquad \ldots(30)$$

Comparing equations (24) and (30) we obtain for the thermal conductivity

$$K = \frac{1}{3}v^2\tau\, C_v = \frac{1}{3}\ell v C_v \qquad \ldots(31)$$

From equation (23) and (31) we obtain

$$\frac{K}{\sigma} = \frac{C_v m_e v^2}{3ne^2} \qquad \ldots(32)$$

Applying classical gas laws we get, $C_v = \frac{3}{2}m_e v^2 = \frac{3}{2}k_B T$ where k_B is Boltzmann's constant. Hence equation (32) reduces to

$$\frac{K}{\sigma} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 T \qquad \ldots(33)$$

Thus the ratio of the thermal and the electrical conductivity is proportional to T and the proportionality constant depends only on the universal constants k_B and e. This result agrees with the Wiedemann-Franz law. The ratio $\frac{K}{\sigma T}$, known as Lorenz number, is found from equation (33) to be

$$\frac{K}{\sigma T} = \frac{3}{2}\left(\frac{k_B}{e}\right)^2 = 1.11\times10^{-8}\ V^2/K^2 \qquad \ldots(34)$$

This value is about one half the typical value for most metals. Although the classical laws cannot be applied to the electron ga in a metal, excellent agreement of the Lorenz number with experiments, apart from the factor of 2, is obtained because of cancellation of errors in the electronic contribution to the heat capacity C_v and the mean square electron speed.

Density of states for free electron gas:

For electrons in a metal or gas molecules in a container, the value of l is so large that the energy levels can be regarded as forming a continuous spectrum. For this case determine the number of states (n_x, n_y, n_z) with energies in the interval between E and E + dE.

Soln. The problem here is very similar to that of the blackbody problem . Writing $N = \sqrt{n_x^2 + n_y^2 + n_z^2}$; we obtain for the number of states, dS, with energies between E and E + dE

$$dS = \frac{1}{8}\left(4\pi N^2 dN\right) = \frac{\pi}{2} N^2 dN$$

From energy of cubic box, $N^2 = n_x^2 + n_y^2 + n_z^2 = E\left(\frac{8m\ell^2}{h^2}\right)$

So, that $$N = \left(\frac{8m\ell^2}{h^2}\right)^{1/2} E^{1/2} \qquad dN = \left(\frac{8m\ell^2}{h^2}\right)^{1/2} \frac{dE}{dE^{1/2}}$$

And, $$dS = \frac{\pi}{2} E \left(\frac{8m\ell^2}{h^2}\right)\left(\frac{8m\ell^2}{h^2}\right)^{1/2}\left(\frac{dE}{2E^{1/2}}\right) = \frac{2\pi\ell^3 (2m)^{3/2}}{h^3} E^{1/2} dE$$

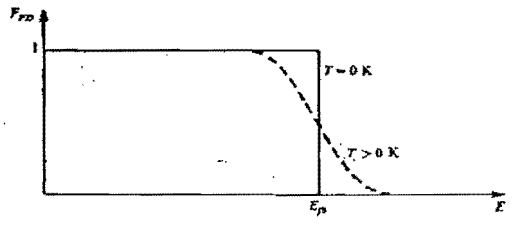
Thus, the density of states in the energy interval dE is, with $V = \ell^3$.

$$g(E) = \frac{2\pi V (2m)^{3/2}}{h^3} E^{1/2}$$

Fermi Distribution function graph:

Near $T = 0K$, $E_f \approx E_{f0} > 0$, and so $F_{FD} \approx \frac{1}{e^{(E-E_{f0})/kT} + 1}$

If $E < F_{f0}$ and $T \to 0K$, $e^{(E-E_{f0})/kT} \to 0$ and $F_{FD} = 1$. If $E > F_{f0}$ and $T \to 0K$, $e^{(E-E_{f0})/kT} \to \infty$ and $F_{FD} = 0$. Therefore the graph of F_{FD} against E has the form given by the solid curve in figure below. If $T > 0K$ it is found that the graph takes on the form given by the dashed curve.



Fermi energy at T = 0

The density of states between energy E and E + dE is:

$$dS = g(E)dE = \frac{2\pi V(2m)^{3/2}}{h^3} E^{1/2} dE$$

Since for each set of quantum numbers (n_x, n_y, n_z) there are two possible electron spin orientations, we must multiply g(E) by a factor of 2 to get the actual density of states for the electron gas. Thus, the total number N of fermions in the system is given by

$$N = 2\int_0^\infty F_{FD} g(E) dE = \frac{4\pi V(2m)^{3/2}}{h^3} \int_0^\infty \frac{E^{1/2} dE}{e^{(E-E_{f0})/kT} + 1}$$

At T = 0K the Fermi-Dirac distribution function is

$F_{FD} = 1$ for $E < E_{f0}$;

$F_{FD} = 0$ for $E > E_{F0}$

So, the limits on the integral can be changed, to give

$$N = \frac{4\pi V(2m)^{3/2}}{h^3} \int_0^{E_{f0}} E^{1/2} dE = \frac{4\pi V(2m)^{3/2}}{h^3} \left(\frac{2}{3} E_{f0}^{3/2}\right)$$

Or,
$$E_{f0} = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}$$

Density of states in Photon gas:

Consider, for simplicity, a cubic cavity of side *l* whose edges define a set of axes and whose walls are maintained at a temperature T. Maxwell's equations for electromagnetic waves show that the rectangular components of the wave vector.

$$k = \frac{2\pi}{\lambda^2}\lambda$$

must satisfy the boundary conditions,

$$\frac{k_x \ell}{\pi} = n_x, \qquad \frac{k_y \ell}{\pi} = n_y, \qquad \frac{k_z \ell}{\pi} = n_z$$

where n_x, n_y, and n_z are positive integers. (These boundary conditions ensure an integral number of half waves in each edge of the cube.) Each triplet (n_x, n_y, n_z) represents, in classical terms, an electromagnetic mode of oscillation for the cavity; we shall consider these modes as photon states. Find the number of modes in the frequency interval between v and v + dv, given that there are two independent polarization directions for each mode.

Soln. Each allowed freuqency v corresponds to a certain mode (n_x, n_y, n_z) and can be written as

$$v = \frac{c}{\lambda} = \frac{ck}{2\pi} = \frac{c}{2\ell}\sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{cN}{2\ell}$$

where $N = \sqrt{n_x^2 + n_y^2 + n_z^2}$. Instead of trying to find the number of integer states (n_x, n_y, n_z) corresponding to a given N, we use a continuous approximation and find the number of points in a spherical shell of radius N

and thickness dN in the first octant of (n_x, n_y, n_z) space. This is the "volume".

$$dM = \frac{1}{8}\left(4\pi N^2 dN\right) = \frac{\pi}{2}N^2 dN$$

But the number of states between N and N+dN must equal the number of states in the corresponding frequency interval, v to v + dv. Using $v = cN/2\ell$

$$dN = \frac{2\ell}{c}dv$$

From which $$dM = \frac{\pi}{2}\left(\frac{2\ell v}{c}\right)^2\left(\frac{2\ell}{c}dv\right) = \frac{4\pi\ell^3}{c^3}v^2 dv = g(v)dv$$

Thus, the density of photon states in a frequency interval dv is

$$g(v) = \frac{8\pi V}{c^3}v^2$$

Example: Show that the kinetic energy of a three dimensional gas of N free electrons at 0 K is

$$E_0 = \frac{3}{5}NE_{F(0)}$$

Soln. Average K.E. of an electron E_0 if given by an expression

$$\bar{E}_0 = \frac{1}{N}\int_0^\infty E.g(E)\cdot f(E)dE$$

Where $g(E) = c\sqrt{E}$ and using the result, $f(E) = 1$ for $E < F_0$ and $f(E) = 0$ for $E < F_0$ at $T = 0$ K, we get

$$\bar{E}_0 = \frac{1}{N}\int_0^{E_{F(0)}} E.C\sqrt{E}dE + \frac{1}{N}\int_{E_{F(0)}}^\infty E.C\sqrt{E}.0.dE = \frac{2}{5}\frac{C}{N}E_{F(0)}^{5/2} \qquad \ldots (1)$$

Now $CE_{F(0)}^{1/2} = g(E_{F_0})$ and $g(E_{f(0)}) = \frac{3}{2}\frac{N}{E_{F(0)}}$

Combining the two , we get $CE_{F(0)}^{1/2} = \frac{3}{2}\frac{N}{E_{F(0)}}$ or $\frac{C}{N} = \frac{3}{2}\frac{1}{E_{F(0)}^{3/2}}$

$$\bar{E}_0 = \frac{2}{3}\cdot\frac{3}{2}\frac{1}{E_{F(0)}^{3/2}}E_{F(0)}^{5/2} \qquad \ldots (2)$$

Substituting (2) in (1) we get, $\bar{E}_0 = \frac{3}{5}E_{F(0)}$

$\therefore$ Kinetic energy of N free electron $= \frac{3}{5}NE_{F(0)}$

Property	1-D	2-D	3-D
(i) Fermi energy[E_F]	$\frac{\hbar^2}{2m}\left(\frac{N\pi}{2L}\right)^2$	$\frac{\hbar^2\pi N}{mA}$	$\frac{\hbar^2}{2m}\left(\frac{3\pi^2N}{V}\right)^{2/3}$
(ii) Density of state[D(E)]	$\frac{4L}{\hbar}\left(\frac{m}{2E}\right)^{1/2}$	$\frac{mA}{\hbar^2\pi}$	$\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}E^{1/2}$
(iii) Average K.E.[E]	$\frac{1}{3}NE_F$	$\frac{1}{2}NE_F$	$\frac{3}{5}NE_F$
(iv) Fermi wave vector[k_F]	$\left(\frac{N\pi}{2L}\right)$	$\left(\frac{2\pi N}{A}\right)^{1/2}$	$\left(\frac{3\pi^2N}{V}\right)^{1/3}$
(v) Fermi velocity[V_F]	$\frac{\hbar}{m}\left(\frac{N\pi}{2L}\right)$	$\frac{\hbar}{m}\left(\frac{2\pi N}{A}\right)^{1/2}$	$\frac{\hbar}{m}\left(\frac{3\pi^2N}{V}\right)^{1/3}$

- $E_F=\frac{P_F^2}{2m}$, $P_F=\hbar k_F$, $v_F=\frac{P_F}{m}$, $T_F=\frac{E_F}{k_B}$

Example: Na metal with bcc structure has radius of Na atom to be 1.85Å. Calculate
(a) Fermi energy, fermi velocity
(b) Electrical resistivity from a Drude model. $\tau=3\times10^{-14}$ sec.

Soln. Electrical conductivity $\sigma=\frac{ne^2\tau}{m}$

$$\text{Since, } n=\frac{2}{a^3}=\frac{3\sqrt{3}}{32r^3} \quad \Rightarrow \quad \sigma=\frac{3\sqrt{3}}{32r^3}\times\frac{\left(1.6\times10^{-19}\right)^2\times3\times10^{-14}}{9.1\times10^{-31}}$$

$$\text{Fermi energy } E_F=\frac{\hbar^2}{2m}\left(\frac{3\pi^2N}{V}\right)^{2/3}=\frac{\hbar^2}{2m}\left(\frac{6\pi^2}{a^3}\right)^{2/3}$$

Example: Cu has fcc lattice of dimension 3.61 Å each atom contributing a single electron to electrical conductivity σ. Given the value at 300K. $\sigma=6.25\times10^7\ \Omega^{-1}m^{-1}$. Estimate
(a) The density of conduction electrons.
(b) Using the Drude model the relaxation time for electron.
(c) The mean path λ assuming that electron behave as a classical ideal gas at 300 K.

$a=3.61\text{Å}$, $\quad \sigma=6.25\times10^7$

Soln. (a) $$n=\frac{N}{v}=\frac{4\times1}{a^3}=\frac{4}{(3.61)^3\times10^{-30}}=8.5\times10^{28}/m^3$$

(b) $\sigma = \frac{ne^2\tau}{m} \Rightarrow 6.25\times10^7 = \frac{4\times\left(1.6\times10^{-19}\right)\tau}{(3.61)^3\times10^{-30}\times9.1\times10^{-31}}$,

$$\Rightarrow \tau = \frac{6.25\times10^7\times9.1\times10^{-31}\times(3.61)^3\times10^{-30}}{2\times\left(1.6\times10^{-19}\right)} = 9.45\times10^{-14}\ \text{sec}$$

(c) $\tau = \lambda V_d$

Since, $V_d = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3\times1.38\times10^{-23}\times300}{9.1\times10^{-31}}} \Rightarrow \lambda = \frac{\tau}{V_d}$

Example: Specifify heat at low temperature is dominated by

(a) Core electron (b) Conduction electron

(c) Lattice vibration (d) None of these

Ans. **(b)**

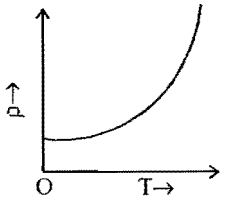
Example: Graph shown is for

(a) Semiconductor

(b) Metal

(c) Super conductor

(d) None of these



Ans. **(b)**

Example: Consider a metal box of length 10 cm and square cross section of 1 cm^2, it has a resistivity and electron density of $10^{-8}\ \Omega-m$ and $2\times10^{28}/m^3$ respectively. A potential difference of 1 V is applied across the metal box. Using Drude model calculate the relexation time (The average time between electron collisions) τ

Soln. $\rho = 10^{-8}\ \Omega-m$

$$n = \frac{N}{V} = 2\times10^{28}\ /m^3$$

Since, $\frac{ne^2\tau}{m} = \frac{1}{\rho} \Rightarrow \tau = \frac{m}{ne^2\rho} = \frac{9.1\times10^{-31}\text{kg}}{2\times10^{28}\times\left(1.6\times10^{-19}\right)^2\times10^{-8}}\text{sec.}$

Example: Copper has a mass density $\rho_m = 8.95\ gm/cm$ and an electricalresistivity $\rho = 1.55\times10^{-8}\,ohm-m$ at room temperature. Calculate

(a) The concentration of conduction electron.

(b) The Mean free time τ

(c) The fermi energy E_F

(d) The fermi velocity V_F

(e) The mean free path λ_F at fermi level.

Soln. (a) 1gm of Cu weighs 64 gms and its volume V is $64/cm$ and its contains Avogadro no. 6.06×10^{23} atom. Hence concentration of conductive e's (assuming valency of copper to be 1) is $\frac{N}{V}=\frac{1\times6.06\times10^{23}\times8.95}{64}=8.47\times10^{23}/cm^3$

(d) If k_F is the fermi wave vector, the fermi energy $E_{F(0)}$ is given by

$$\left(\frac{hk_F}{2m}\right)^2=E_{f(0)}=\frac{h^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{2/3}\Rightarrow K_F=\left(\frac{3\pi^2N}{V}\right)^{1/3}=\left(29.609\times8.47\times10^{22}\right)^{1/3}=1.358\times10^8cm^{-1}$$

The fermi velocity

$$V_f=\frac{hk_F}{m}=1.157\times k_f=1.157\times1.358\times10^8cm/sec.=1.566\times10^8\,cm^{-1}$$

(c) Fermi energy $E_{f(0)}=\frac{1}{2}mv_f^2=0.284\times10^{-15}v_f^2$ mi ev. = 7.0 eV.

(b) Fermi temperature $T_f=E_f/k=8.12\times10^4k$

electrical resistivity $\ell=\frac{1}{\sigma}=\frac{m}{ne^2\tau(E_f)}$

Since, $\ell=1.55\times10^{-8}\Omega-m$, $m=9\times10^{-31}$ kg., $e=1.6\times10^{-19}c$ and $n=\frac{N}{V}=8.47\times10^{28}/m^3$

Thus $\tau(E_f)=\frac{m}{ne^2\ell}\Rightarrow\tau(E_f)=2.677\times10^{-14}$ sec

(e) The Mean free path λ_F of a conductorial electron in defined as

$$\lambda_F=V_F\tau(E_f)=1.566\times10^8\times(2.677\times10^{-14})=4.891\times10^{-6}\text{ cm}$$

Example: Show that if the mean free path is independent of the velocity, the electrical conductivity of Maxwell-Boltzmann free electrical gas may be expressed as.

$$\sigma=\frac{4}{3}\frac{ne^2\lambda}{\sqrt{2\pi mkT}}$$

Soln. When λ and τ are independent of velocity the M.B distributive give avg value of $\bar{\tau}$ as.

$$\bar{\tau}=\frac{\lambda<v>}{<v^2>}$$

But kinetic theory and law of equipartition of energy gives $\frac{1}{2}m<v^2>=\frac{3}{2}kT\Rightarrow<v^2>=\frac{3kT}{m}$

Hence $\bar{\tau}=\frac{\lambda\bar{c}}{3kT/m}=\frac{\lambda\bar{c}^2}{3kT/m\times\bar{c}}$

But $\bar{c}^2=\frac{8kT}{\pi m}\Rightarrow\bar{\tau}=\frac{\lambda.8kJ/\pi m}{3TK/m\bar{c}}=\frac{8\lambda}{3\pi\bar{c}}$

Now $\sigma=\frac{ne^2\bar{\tau}}{m}\Rightarrow\sigma=\frac{ne^2.8\lambda}{3\pi m\bar{c}}=\frac{ne^2.8\lambda}{3\pi m\sqrt{8kt/\pi m}}=\frac{8ne^2\lambda}{3\times2\sqrt{2\pi kTm}}=\frac{4}{3}\frac{ne^2\lambda}{\sqrt{2\pi mkT}}$

Example: Calculate the drift mobility and mean scattering time of conduction e's in copper at room temp., given that conductivity of copper is $5.9\times10^{5}\Omega^{-1}cm^{-1}$, density of copper is 8.96 gm cm^{-3} and its atomic mass is 63.5 g mol^{-1}

Soln. $n=\frac{dN_A}{Mat}$ $\qquad n=8.5\times10^{22}e/cm^3$

$\mu_d=\frac{\sigma}{en}=43.4\ cm\ v^{-1}s^{-1}$ $\qquad\Rightarrow\ \tau=\frac{\mu_d m_e}{e}=2.5\times10^{-14}\ sec$

Example: What is the applied electric field that will impose a drift velocity equal to 0.1 % of the mean speed u ($=10^6\ ms^{-1}$) of conduction in coppers. What is the corresponding current density and current through a Cu wire of dia 1 mm ?

Soln. $V_d=\mu_d E_x$ $\qquad \mu_d(cu)=43.4\ cm^2v^{-1}s^{-1}$, $\qquad V_{d_x}=0.001u=10^3ms^{-1}$

$E_x=\frac{V_{dx}}{\cos\theta}=2.3\times10^5 vm^{-1}$ or $230\ kvm^{-1}$

$J_x=\sigma E_x=\left(5.9\times10^7\right)\left(2.3\times10^5\right)=1.4\times10^{13}\ Am^{-2}$

Example: Calculate the fermi energy E_{F0} at ok for Cu and estimate the ave. speed of the conductium e's is Cu. Density of Cu is 8.96 gm cm^{-3} . At . mass = 63.5

Soln. $n=\frac{dN_A}{Mat}=8.5\times10^{28}m^{-3}$

$E_{F(0)}=\left(\frac{h^2}{8m_e}\right)\left(\frac{3n}{\pi}\right)^{2/3}$

$E_{F(0)}=1.1\times10^{-18}J.$

$\frac{1}{2}m_e v_e^2=\frac{3}{5}E_{F_0},\quad V_e=\sqrt{\frac{6E_{F0}}{5me}},\quad V_e=1.2\times10^6 ms^{-1}$

Example: Compute the fermi energy for sodium, assuming that each sodium atom contributes one free electron to the electron gas. The density of sodium in 0.971 gm/cc and its at. wt. is 23.

$\left(h=6.63\times10^{-34}\text{Joule}-\text{sec}\right)$, $M=9.11\times10^{-31}kg$ and Avogadro's no: – 6.02×10^{23} atoms/mole).

Soln. Let V = vol. of piece of Na.
N = No. of free e's in it
∴ free electron density = N/V = No. of Sodium atoms per unit volume

because each Na atom contributes one free e^- to the gas.

No. of molecules per unit volume

$=\frac{N_A}{M/\ell}=\frac{N_A\ell}{M}=\frac{\left(6.02\times10^{23}\right)(0.971)}{23}=2.54\times10^{28}\ electrons/m^3$

Fermi energy for sodium is

$$E_F = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3} = \frac{\left(6.63\times10^{-34}\right)}{2\left(9.11\times10^{-31}\right)}\left(\frac{3\times2.54\times10^{28}}{8\times3.14}\right)^{2/3} = 5\times10^{-19}\,J \text{ or } \frac{5\times10^{-19}}{1.6\times10^{-19}} = 3.1eV$$

Example: There are 2.54×10^{22} free electrons per in Na. Calculate the fermi energy. Fermi velocity and Fermi temperature. ($h = 6.63 \times 10^{-3}$ J, $M = 9.11 \times 10^{-31}$ kg, $k = 1.38 \times 10^{-23}$ joule/k 1eV = 1.6×10^{-19} Joule).

Soln. $E_F = \frac{h^2}{2m_e}\left(\frac{3N}{8\pi V}\right)^{2/3}$

Given $\frac{N}{V} = 2.54\times10^{22}/cm^3 = 2.54\times10^{28}/m^3$,

$E_F = 5 \times 10^{-19}$ Joule = 3.1 eV.

This is the maximum kinetic energy of free electron at absolute zero. If V_F be the fermi velocity then

$$\frac{1}{2}mv_f^2 = E_F = 5\times10^{-19}\,\text{Joule} \quad \Rightarrow v_F = \sqrt{\frac{2\times5\times10^{-19}}{9.11\times10^{-31}}} = 1.05\times10^6\,m$$

$$\therefore \text{Fermi Temperature } T_F = \frac{E_F}{k} = \frac{5\times10^{-19}}{1.38\times10^{-23}} = 3.6\times10^4 k$$

Example: The Density of Zinc ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s$) is 7.13 gm/cm^3 and its at. wt is 6.54 . Calculates its fermi energy . The effective mass of a free electron in Zn Crystal is 7.7×10^{-31} kg and the Avogadro's number is 6.02×10^{23} atoms /gm-at.
Each atom has 2 valence electron which it contributes to the electron gas.

Soln. The mass of 1 gm -atom of Zn is 65.4 gm, so that the volume $v = \frac{\text{mass}}{\text{density}} = \frac{65.4}{7.13} = 9.17cm^3$.

The no. of Zn atoms in this volume is 6.02×10^{23}.

$$\therefore \text{No. of atoms per unit volume} = \frac{6.02\times10^{23}}{9.17} = 6.56\times10^{22}/cm$$

$$\frac{N}{V} = 2\times6.56\times10^{22} = 13.1\times10^{28}/m^3$$

$$E_F = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3} = 11\,eV$$

Example: The Fermi energy for silver is 5.51 eV (a) What is the average energy of the free electron in silver at 0K? (b) At what temperature a classical free particle (such as ideal gas molecule) will have this kinetic energy?
($k = 1.38 \times 10^{-23}$ J/K and 1 eV = 1.6 $\times 10^{-19}$ Joule)

Soln. (a) $\bar{\varepsilon}_0 = \frac{3}{5}E_F = \frac{3}{5}\times5.51 = 3.306$ eV

(b) K.E = 3/2 KT = 3.306 eV = $3.306 \times 1.6 \times 10^{-19}$ J

$$\therefore T = \frac{2}{3}\times\frac{3.306\times1.6\times10^{-19}}{1.38\times10^{-23}} = 2.55\times10^4 k$$

Example: The Fermi energy for Lithium is 4.72 eV at absolute zero. Calculate the No. of conduction electrons per unit volume in Lithium.
($h = 6.63 \times 10^{-34}$ J-sec, $m = 9.11 \times 10^{-31}$ kg)

Soln. $E_F = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3} \quad \Rightarrow \frac{N}{V} = \left(\frac{2m}{h^2}\right)^{3/2} \cdot E_F^{3/2} \cdot 8\pi/3 = 4.64 \times 10^{28}/m^3$

Example: Calculate mean free path (λ_F), Fermivelocity (V_F) and characteristic time (τ_F) for cooper of resistivity $1.7 \times 10^{-8}\ \Omega - m$, e^- – concentration $8.5 \times 10^{26}\ e^-/m^3$ and Fermi energy $E_F = 7.01$ eV.

Soln. $\frac{1}{2}mV_F^2 = V_F^2 = \frac{2E_F}{m} = \frac{2 \times 7.01 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}} = 2.5 \times 10^{12}$

$V_F = 1.56 \times 10^6$ m/sec

$\tau_F = \frac{m}{ne^2\rho} = \frac{9.1 \times 10^{-31}}{8.5 \times 10^{28} \times \left(1.6 \times 10^{-19}\right)^2 \times 1.7 \times 10^{-8}} = 2.4 \times 10^{-14}$ sec

$\lambda_F = V_F \tau_F = 37.8$ nm

Example: Take the fermi energy of silver to be 5.5eV.
(a) Find the corresponding velocity of conduction electrons. (valence electrons)
(b) If the resistivity of silver at room temperature is $1.62 \times 10^{-8}\ \Omega - m$, estimate the average time between successive collisions.
(c) Also determine the mean free path
(d) Determine the zero point energy per electron in silver.
(e) Determine the fermi temperature.
(f) Determine the diameter of fermi surface.

Soln. (a) $E = \frac{\hbar^2}{2m}\left(\frac{2\lambda^2 N}{V}\right)^{2/3} = 5.5eV \quad \Rightarrow \left(\frac{3\lambda^2 N}{V}\right)^{2/3} = 5.5 \times \frac{2m}{\hbar^2}$

$= \frac{5.5 \times 2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19}}{1.05 \times 10^{-34} \times 11.05 \times 10^{-34}} = 145.27 \times 10^{18}$

$\therefore K_F^2 = 145.27 \times 10^{18} m^{-1} \quad \Rightarrow K_F = 1.20 \times 10^{10}\ m^{-1}$

$\therefore V_F = \frac{\hbar K_F}{m} = \frac{1.05 \times 10^{-34} \times 1.20 \times 10^{10}}{9.1 \times 10^{-31}} m/s \quad = 0.138 \times 10^7\ m/s \quad = 1.38 \times 10^6\ m/s$

(b) $\rho = \frac{1}{\sigma}$ and $\sigma = \frac{ne^2\tau}{m}$ where n = electron concentration

$K_F = \left(3\lambda^2 n\right)^{1/3} = 1.20 \times 10^{10}\ m^{-1} \quad \Rightarrow 3\lambda^2 n = \left(1.20 \times 10^{10}\right)^3 = 1.728 \times 10^{30}$

$\Rightarrow n = \frac{1.728 \times 10^{30}}{3\lambda^2} = 5.83 \times 10^{28}/m^3$

$$\therefore \sigma = \frac{ne^2\tau}{m}$$

$$\Rightarrow \tau = \frac{\sigma m}{ne^2} = \frac{m}{n\rho e^2} = \frac{9.1\times10^{-31}}{5.83\times10^{28}\times1.62\times10^{-8}\times\left(1.6\ \ 10^{-19}\right)^2} = 3.76\times10^{-14}\ \text{sec.}$$

(c) $\lambda = v\tau = 1.38\times10^{6}\times3.76\times10^{-14}\ \text{m} = 6.18\times10^{-8}\,\text{m}$

(d) $E_F = \frac{3}{2}E_F(0) = \frac{3}{5}\times5.5\text{eV} = 3.3\text{ev}.$

(e) $K_BT = E_F \Rightarrow T = E_F/K_B = \frac{5.5\times1.6\times10^{-19}}{1.23\times10^{-13}}\text{K} = 7.15\times10^{4}\,\text{K}$

(f) Diameter $= 2K_F = 2.40\times10^{10}\,\text{m}^{-1} = 2.4\text{A}^{o-1}$

Example: Aluminium in trivalent with atomic weight 27 and density 2.7 gm/cm^3. While the mean collision time between electrons is 4×10^{-24} secs calculate

(a) Current flowing through an aluminium wire 20 m long and 2 mm^2 cross-sectional area when a potential of 3V is applied to its ends

(b) Calculate the lattice constant of all

Soln. (a) $\text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{27}{2.7}\text{cm}^3 = 10\text{cm}^3$

In this volume there are 6.023×10^{23} Al atoms

$\therefore$ Number of atoms / volume $= \frac{6.023\times10^{23}}{10}\text{cm}^{-3} = 6.023\times10^{22}\,\text{cm}^{-3}$

$\therefore$ Each atom contributes 3 e$^-$

$\therefore$ Electron contribution $n = 3\times6.023\times10^{22}\,\text{cm}^{-3} = 18.069\times10^{22}\,\text{cm}^{-3}$

Current density $J = neVd = \frac{ne^2\tau E}{m}$

$$= \frac{18.069\times10^{22}\times\left(1.6\times10^{-19}\right)^2\times4\times10^{-10}\times0.15\times10^{-2}}{9.1\times10^{-31}}\text{A/cm}^2$$

Required Current = J $\times$ Area

(b) $a^3 = \frac{nM}{NS} = \frac{4\times27}{6.023\times10^{23}\times2.7}\text{m}^3 = 0.664\times10^{-22}\,\text{m}^3$

$\therefore\ a = 4.049\times10^{-8}\,\text{m} = 4.049\text{A}^0$

SUMMARY

1. According to the free electron gas model, the valence electrons of the atoms present in a metal move freely among the positive ion cores just like the molecules of an ideal gas. These electrons are also called the conduction of electricity.

2. The energy spectrum of a free electron gas present in one or thre-dimensional box is descrete particularly when the box has atomic dimensions. For laboratory dimensions, the levels almost form a continum. The allowed eigen values of the states with wave vector k are given as

$$E_k = \frac{h^2k^2}{2m} = \frac{h^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

where m is the mass of the electron.

3. The fermi level is the level which divides the filled and unfilled states. It is the topmost filled level at 0 K. For T>0, the probability of occupation of this level is 1/2. The positin of the Fermi level changes with temperature and is expressed by the relation.

$$E_F = E_{F_0}\left[1 - \frac{\pi^2}{12}\left(\frac{k_BT}{E_{F_0}}\right)^2\right]$$

where E_{F_0} is the Fermi energy at 0 K.

4. The Fermi energy varies with electron concentration n as

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2 n\right)^{2/3}$$

5. The number of electronic states present in a unit energy range is called the density of states. In a three-dimensional box of volume V, the density of states at energy E is given by

$$D(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

At the Fermi level, D(E) may be expressed as

$$D(E_F) = \frac{3}{2}\frac{N}{E_F}$$

where N is then total number of electrons.

6. The avearge kinetic energy of an electron at 0 K is related to the Fermi energy at the same temperature as

$$\bar{E}_0 = \frac{3}{5}E_{F_0}$$

7. The free electron gas model explains the electronic specific heat of metals by restricting the number of electrons contributing to specific heat to $N\left(\frac{k_BT}{E_F}\right)$. It yielded the expression for specific heat as

$$C_v \cong \frac{3}{2}Nk_B\left(\frac{k_BT}{E_F}\right)$$

Chapter-7: MAGNETIC PROPERTIES OF MATERIALS

Response of substance of magnetic field:

A magnetic field can be described by either magnetic induction B (or magnetic flux density) or the field strength H. In vacuum, they are related by the equation

$$B = \mu_0 H \qquad \ldots (1)$$

where $\mu_0 = 4\pi \times 10^{-7}\ H - m^{-1}$ and is called the permeability of the free space (vacuum).

When a substance is placed in a magnetic field, it gets magnetized and hence a magnetization M(defined as the magnetic moment per unit volume, i.e. $M = \mu_m / \Delta V$) is produced in it. The magnetic induction inside the substance is given by

$$B = \mu_0 H + \mu_0 M = \mu_0 (H + M) \qquad \ldots (2)$$

where the first term on the right side of equation (2) is due to external field and the second term is due to the magnetization. For an isotropic medium, M and H are parallel vectors and are related to each other according to the relation

$$M = \chi H \qquad \ldots (3)$$

where χ is the susceptibility of the medium and is a scalar quantity. Substituting the value of M from equation (3) into equation (2), we have

$$B = \mu_0 (1 + \chi) H = \mu H \qquad \ldots (4)$$

where $$\mu = \mu_0 (1 + \chi) \qquad \ldots (5)$$

is known as the permeability of the medium. It is often more convenient to use the relative permeability μ_r, which is defined as

$$\mu_r = \frac{\mu}{\mu_0} = (1 + \chi) \qquad \ldots (6)$$

Example: The applied magnetic field in copper is 10^6 A/m. If the magnetic susceptibility of copper is -0.8×10^{-5}, calculate the flux density and the magnetization in copper.

Soln. Given: $H = 10^6\ A/m$, $\chi = -0.8 \times 10^{-5}$, $\mu_0 = 4\pi \times 10^{-7}\ H/m$, B = ?, M = ? Making use of equation (3), we have

$$M = \chi H = -0.8 \times 10^{-5} \times 10^6 = -8\ A/m$$

Further, from equation (2) we have

$$B = \mu_0 (H + M) = 4\pi \times 10^{-7} (-8 + 10^6) = 1.256\ T$$

Classification of Magnetic Materials:

Magnetic materials can be classified into different categories according to their χ values and the way in which these vary with the magnetic field strength and temperature. They are: (i) Diamagnetic, (ii) Paramagnetic, (iii) Ferromagnetic, (iv) Antiferromagnetic and (v) Ferrimagnetic.

The Diamagnetic property is the result of an induced magnetic moment. This arises when an atom is placed in a magnetic field. The motion of orbital electrons of the atom (analogous to a current flowing in a circuit) gets modified in such a way that weak magnetic moment opposing the field is induced. Also, if χ is negative in equation (3), the direction of magneticzation M is opposite to that of the field H.

A diamagnetic solid has a tendency to repel the magnetic lines of force due to an external applied field (figure). A superconductor which repels all the lines of force, is an example of a perfect diamagnet.

Diamagnetic substances include inert gases (helium, argon, etc), metals (bismuth, copper, zinc, gold, silver etc.), mercury, water, glass, marble and many other organic compounds. For a diamagnetic substance, the relative permeability μ_r (or the susceptitibility χ) is independent of temperature.

Unlike diamagnetism, paramagnetism and ferromagnetism are the result of intrinsic magnetic moment. Some atoms and ions do posses permanent magnetic moment. In the absence of an external field, these moments are randomly oriented with respect to one another because of thermal fluctuations and therefore the substance exhibits no net magnetic moment. However, when placed in a magnetic field, the moments tend to align along the direction of field, producing a net magnetization. When the atoms and ions are acted upon individually, with no mutual interaction between them, the effect is called paramagnetism. Since the moments line up in the direction of the field which help enhance the external field, the paramagnetic susceptibility is greater than zero. Further, because of small paramagnetic susceptibility a paramagnetic substance weakly attracts the lines of force. (Figure). As thermal energy randomizes the alignment of the dipoles, the paramagnetic susceptibility decreases with the increase of temperature.

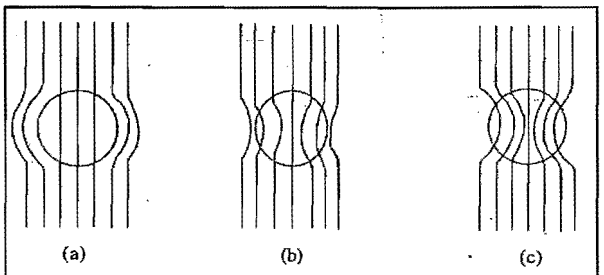


Figure: Behaviour of magnetic lines of force under applied magnetic field in (a) Diamagnet (b) Paramagneti and (c) Ferromagnet.

Paramagnetic substances include aluminium, platinum, potassium, manganese, the rare-earth elements, alkali and alkaline earth metals etc.

A ferromagnetic substance possesses permanent (spontaneous) magnetic moments even in the absence of an external magnetic field. Since, the ferromagnetic susceptibility is very large and positive, so that a ferromagnetic substance strongly attracts the lines of force (Figure). Ferromagnetism exists only below a certain temperature T_c, above which the substance becomes paramagnetic.

Ferromagnetic substances include iron, cobalt, nickel and a number of alloys.

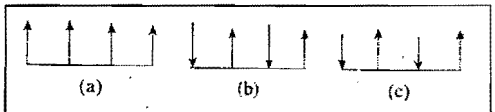


Figure: Magnetic arrangements in (a) Ferromagnet (b) Antiferromagnet and (c) Ferrimagnet

In fully magnetized state of a ferromagnet, all the dipoles are aligned in exactly the same direction (Figure). An antiferromagnetic substances has the dipoles with equal moments, but the alternate dipoles point in opposite directions (Figure). As a result, the moments balance each other and result in a zero net magnetization. Another commonly encountered substance is ferrimagnetic, the moments of which are shown in figure. In this case too, the neighbouring dipoles point in opposite directions but they are unequal. As a result, they do not completely balance each other and posses finite net magnetization.

Atomic theory of magnetism:

In an atom, we know that the electrons revolve round the nucleus in different circular orbits. Analogous to this situation let us consider an electron of mass m, having an electronic charge (–e) moving in a circular orbit of radius 'r' with a velocity v (angular velocity ω) as shown in (Figure .....) From the basic knowledge of current electricity, we know that a moving electron constitutes an electric current, i.e.

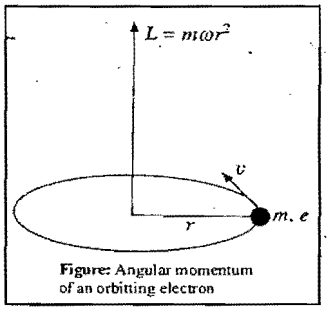


Figure: Angular momentum of an orbitting electron

$$I = \frac{dq}{dt} \text{ and } Ids = \frac{dq}{dt}ds = dq\frac{ds}{dt} = -ev \qquad \ldots(7)$$

where $dq = -e$ and $v = \frac{ds}{dt}$, the linear velocity. But for a circular orbit, $ds = 2\pi r$ and $v = \omega r$, so that

$$I \times 2\pi r = -e\omega r \qquad \Rightarrow I = -\frac{e\omega}{2\pi} \qquad \ldots(8)$$

From electromagnetic theory, it is well known that the magnetic field produced by a current, I flowing in a staionary loop of cross sectional area A at right angles to the plane of the current loop is identical with that produced by a magnetic dipole when measured at large distance (as compared to the radius of the loop). The magnitude of the magnetic moment produced by (the circular motion of the electron) such as a dipole is

$$\mu_m = I.A \qquad \ldots(9)$$

For a circular orbit $A = \pi r^2$, also substituting the value of I from equation (8) into equation (9), we obtain

$$\mu_m = -\frac{e\omega}{2\pi} \times \pi r^2$$

$$\Rightarrow \qquad \mu_m = -\frac{e\omega r^2}{2} = -\frac{em\omega r^2}{2m} = -\left(\frac{e}{2m}\right)L \qquad \ldots(10)$$

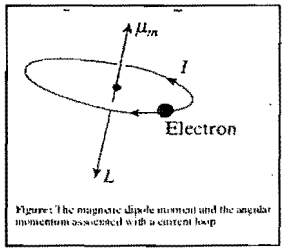


Figure: The magnetic dipole moment and the angular momentum associated with a current loop

where $L = m\omega r^2$ is the orbital angular momentum of electron and is normal to the plane of the orbital. The minus sign in equation (10) indicates that the magnetic moment μ_m is antiparallel to the angular momentum L (figure). This equation is valid only for motion of electron and not for spin of the electron or nucleus.

The origin of permanent magnetic moments:

Permanent magnetic moments can arise from the following three different sources.

1. The orbital magnetic moment of the electrons.
2. The spin magnetic moment of the electrons, and
3. The spin magnetic moment of the nucleus.

1. The orbital magnetic moment of the electrons:

Based on the classical consideration of atomic theory of magnetism, we obtained an expression (equtaion (10)) of magnetic moment ..... However, quantum consideration tells us that the angular momentum vector can take only specific orientation in space (given by equation (13)) when the atom is placed in an external magnetic field. Therefore, with the help of these equations (equations (10)) and (13), we obtain

$$\mu_m = -\left(\frac{e}{2m}\right)L_{\ell,B} = -\left(\frac{e}{2m}\right)m_\ell \hbar = -\left(\frac{eh}{4\pi m}\right)m_\ell$$

$$\Rightarrow \qquad \mu_m = -m_\ell \mu_B \qquad \ldots ( )$$

where $\mu_B = \frac{eh}{4\pi m} = 9.27\times10^{-24}\ A\bar{m}^2$, and is called the Bohr magneton. It is the quantum of orbital magnetic moment and is accepted as one unit for measuring the magnetic moments of atomic systems.

In a complex atom whose shells have many electrons, the total orbital magnetic moment is determined by taking the algebraic sum of the magnetic moments of individual electrons in compliance with the rules. The moment of a completely filled shell is zero and hence an atom with paritially filled shells will have a non zero orbital magnetic moment.

2. The spin magnetic moment of the electrons:

Like orbital magnetic moment, the spin magnetic moment can be determined by substituting the value of magnetic spin angular momentum S from equation (15) into equation (10), we obtain

$$\mu_s = \frac{gm_B}{2} \qquad \ldots (17)$$

That is, the spin magnetic moment is half of a Bohr magneton. This is only approximately correct because equation (10) is not valid for electron spins. In fact, the magnetic moment component μ_{sz} along the field direction is given by

$$\mu_{sz} = g\left(\frac{e}{2m}\right)m_s\hbar = g\left(\frac{eh}{4\pi m}\right)m_s \qquad \ldots (18)$$

where 'g' is called the spectroscopic splitting factor or the Lande's splitting factor. For the electron spin spin g = 2.0023, i.e. the electron spin gives rise very nearly one Bohr magneton in the direction (or opposite) of an external field. The reason for the name "splitting facror" is the following. Consider an electron having no orbital motion, is placed in a magnetic field of induction B. As a result, the electron spin magnet rotates and the potential energy of the magnetic system changes. The potential energy of a magnetic dipole is then given by

$$U = -\mu.B = -\mu B\cos\theta \qquad \ldots (19)$$

Now, since we know tht the magnetic spin quantum number ms can take two values, either $+\frac{1}{2}$ or $-\frac{1}{2}$. It is reasonable to assume that before the application of the field, the electron is in the higher energy state, i.e. $m_s = +\frac{1}{2}$ and after the application of the field it flips over to the lower energy, i.e. $m_s = -\frac{1}{2}$. For the state $m_s = +\frac{1}{2}$, the angular momentum vector is parallel to the field which is seen as antiparallel to the magnetic moment (angle between μ and B is 180°). Accordingly, for the state $m_s = -\frac{1}{2}$, the magnetic moment is parallel to the field (i.e. the angle between μ and B is zero). Making use of this in equation (19) and substituting μ_{sz} for μ (from equation (18), the change in the energy of the electron spin magnetic moment is:

$$\Delta U = 2|\mu_{sz}|B = g\left(\frac{eh}{4\pi m}\right)B = g\mu_B B \qquad \ldots(20)$$

Thus 'g' determines the amount by which the original level splits up under the influence of magnetic field. This is illustrated in figure .....

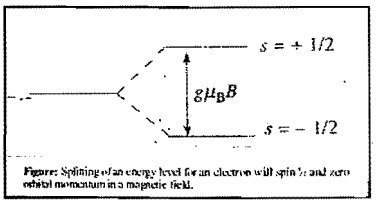


Figure: Splitting of an energy level for an electron with spin ½ and zero orbital momentum in a magnetic field.

Sometimes, the orbital angular momentum L and spin angular momentum S may be combined vectorially to get the total angular momentum J of the whole electron system of the atom. For such atoms, the spectroscopic splitting factor 'g' is given by the Lande formula,

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \qquad \ldots(21)$$

so that the total magnetic moment of the atomic system becomes.

$$\mu = gJ\mu_B \qquad \ldots(22)$$

The values of g and J are known from the spectroscopic data and thus the total magnetic moment of a free atom or ion, in principle, can be determined.

3. The spin magnetic moment of the Nucleus:

Just like an electron, the atomic nucleus possesses intrinsic spin (called nuclear spin) and thus a magnetic moment is the associated with this. Since the nuclear mass is about 10^3 times greater than the mass of an electron, therefore the nuclear magnetic moment is approximately three orders of magnitude smaller than the magnetic moment associated with the electron. As the electron magnetic moment is expressed in the unit of Bohr magneton, similarly the nuclear magnetic moment is expressed in the unit of nuclear magneton. A nuclear magneton is defined as

$$\mu_n = \frac{eh}{4\pi MP} = 5.05\times10^{-27}\ A-m^2 \qquad \ldots(23)$$

where M_p is the mass of a proton.

Langevin's classical theory of diamagnetism:

As we know that the diamagnetism is the occurence of negative susceptibility and the magnetization M in this case is antiparallel to the field (equation (3)). There is no electrical counterpart to the negative susceptibility, although it is vaguely analogous to the depolarization field. The negative susceptibility arises from Lenz's law which states that when the flux in an electrical circuit is changed, an induced current is set up in such a direction as to oppose the flux change. For the following discussion, a circuit will mean the circulating electron in an atom, ion or molecule at a lattice site. Let us consider the Bohr model of atom, i.e. consider an electron which revolves round a central nucleus as shown in figure ( ). If 'm' is the mass of the electron, –e is the charge of the electron 'r' is the radius of the orbit then in the absence of an external field the centripetal force acting on the electron due to the nucleus is given by

$$F_0 = \frac{mv^2}{r} = m\omega_0^2 r \qquad \ldots(24)$$

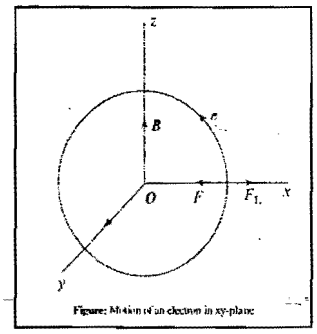


Figure: Motion of an electron in xy-plane

where $v = \omega_0 r$. When a magnetic field is applied along the z-axis (perpendicular to the xy-plane), an additional force F_L equal to the Lorentz force starts acting on the electron in a direction away from the centre. The Lorentz force is given by

$$F_L = -e(v \times B) = -eBr\omega \qquad \ldots (25)$$

where the magnetic field B is perpendicular to r. Because of the change in the net force on the electron, there is a change in the angular frequency from ω_0 to ω. The resulting equation can be written as

$$F_0 - eBr\omega = m\omega^2 r \qquad \ldots (26)$$

Substituting F_0 from equation (24) into equation (26) and solving for ω, we obtain

$$\omega^2 + \frac{eB}{m}\omega - \omega_0^2 = 0$$

So that $$\omega = \pm\left[\left(\frac{eB}{2m}\right)^2 + \omega_0^2\right]^{1/2} - \frac{eB}{2m}$$

If $\omega_0 >> \left(\frac{eB}{2m}\right)$ then $\left(\frac{eB}{2m}\right)^2$ term can be neglected, therefore,

$$\omega = \pm\omega_0 - \frac{eB}{2m} = \pm\omega_0 - \omega_L \qquad \ldots (27)$$

where the change of frequency $\omega_L = \pm\omega_0 - \frac{eB}{2m} = \pm\omega_0 - \omega_L$

where the change of frequency $\omega_L = eB/(2m)$ is called the precessional frequency or Larmour frequency. The $(\pm)$ sign on ω_0 implies that those electrons whose orbital moments are parallel to the field are slowed down by ω_L. In this case, $\omega = \omega_0 - \omega_L$. Similarly those electrons whose moments are antiparallel to the field are speeded up by the same amount. In this case, $\omega = -\omega_0 - \omega_L$.

The change in the frequency of the electronic motion as a result of the application of the magnetic field produces magnetization. Actually, in the absence of the field the electron motion being spherically symmetrical and produces no net current or flux. On the other hand, in the field, the electron's motion is no longer spherically symmetric but precesses about the field (i.e. the plane of the orbit does not remain stationary) and produces a net current I. Due to the change in frequency ω_L, the current for each electron can be written as

$$I = (\text{Charge}) \times (\text{Revolution per unit time}) = -\frac{e\omega_L}{2\pi} = -\frac{e^2 B}{4\pi m}$$

If each atom contains Z electrons then the current becomes

$$I = -\frac{Ze^2\ B}{4\pi m} \qquad \ldots (28)$$

Making use of equation (9), the magnetic moment could be written as

$$\mu_m = -\frac{Ze^2 B}{4\pi m}\pi \bar{p}^2 \qquad \ldots (29)$$

where $\bar{p}^2$ is the mean square radius of the projection of the orbit on a plane perpendicular to the field axis. (Figure). As the field is acting parallel to the z-axis, therefore,

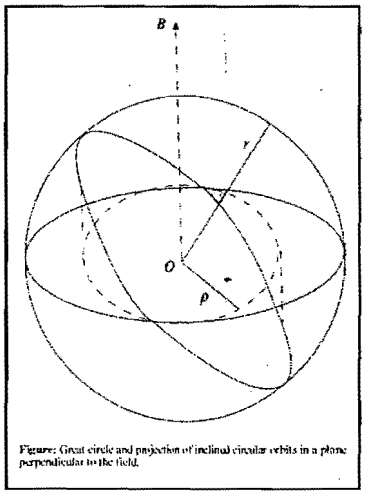


Figure: Great circle and projection of inclinal circular orbits in a plane perpendicular to the field.

$$\bar{p}^2 = \bar{x}^2 + \bar{y}^2$$

The mean square distance (average radius) of the electron from the nucleus is

$$\bar{r}^2 = \bar{x}^2 + \bar{y}^2 + \bar{z}^2 \qquad \ldots (30)$$

Now, for spherically symmetric charge distribution, we have

$$\bar{x}^2 = \bar{y}^2 = \bar{z}^2$$

Here, average is used because all the electrons in an atom do not have the same effective radii, so that

$$\bar{p}^2 = \frac{2}{3}\bar{r}^2 \qquad \ldots (31)$$

This result expresses the fact that the projected area of the great circle titled with respect to the equatorial plane is less than πr^2 as shown in figure. Thus from equation (29) and (31), we obtain

$$\mu_m = -\frac{Ze^2 B\pi \frac{2}{3}\bar{r}^2}{4\pi m} = -\frac{Ze^2 B\bar{r}^2}{6m} \qquad \ldots (32)$$

If N is the number of atoms per unit volume, then the magnetization M is given by $M = N\mu_m$ (also making use of the fact that $B = \mu_0 H$), the diamagnetic susceptibility per unit volume is:

$$\chi_{dia} = \frac{M}{H} = -\frac{\mu_0 Ze^2 N\bar{r}^2}{6m} \qquad \ldots (33)$$

This is the classical Langevin equation for diamagnetism. From equation (33), it is clear that the diamagnetic susceptibility is proportional to N implying that the diamagnetic susceptibility depends on the size of the atom. We also observe that χ_{dia} is proportional to $\bar{r}^2$, meaning thereby that the outer electrons make the largest contribution to the diamagnetic susceptibility.

For normal solids, we may take $N = 5\times10^{28}\ m^{-3}, \bar{r}^2 = 10^{-20}\ m^2$ and substituting them into equation (33) along with the values of other constant quantities, the above equation reduces to

$$\chi_{dia} = Z\times10^{-7} \qquad \ldots (34)$$

This shows the temperature invariance of diamagnetic susceptibility. Diamagnetism is common to all elements, however usually it is too weak to be detected in para and ferromagnetic cases.

Example: Estimate the order of the diamagnetic susceptibility of copper by assuming that only one electron per atom makes the contribution. The radius of the copper atom is 1Å and the lattice parameter is 3.608Å.

Soln. Given: $r = 1\ Å = 10m, a = 3.608\times10^{-10}m, \chi_{dia} = ?$

We know that copper is a face centred cubic crystal, so it has 4 atoms per unit cell. The number of electrons per unit volume can be found as

$$N = \frac{n}{a^3} = \frac{4}{\left(3.608\times10^{-10}\right)^3} = 8.5\times10^{28}/m^3$$

Now making use of equation (35) and substituting the different values, we obtain

$$\chi_{dia} = -\frac{\mu_0 Ze^2 N\bar{r}^2}{6m} = -\frac{4\pi\times10^{-7}\times8.5\times10^{28}\times\left(1.6\times10^{-19}\right)^2\times10^{-20}}{6\times9.1\times10^{-31}} = -5\times10^{-6}$$

Sources of paramagnetism:

As we know that paramagnetism is the case of a positive magnetic susceptibility. It is the magnetic analogue of the electrical orientational polarizability and is due to the permanent magnetic moment of the atoms. The direction of the magnetization is parallel to the external applied field in paramagnetic substances. Paramagnetism (positive contribution to χ) is found in:

1. Atoms, molecules and lattice defects having an odd number of electrons; that is there should be at least one electron which does not pair. The atoms of the group I, III, V and VII of the periodic Table, gaseous nitric oxide(NO); organic free radicals such as triphenylmethyl $C(C_6H_5)_3$ and F-centres in alkali halides, satisfy this criterion.
2. Free atoms with unfilled innershell: transition elements (Z = 57–72) and (Z = 91 –102), rare earth and actinite elements have atoms with unfilled inner shells.
3. A few compounds with an even number of electrons including molecular oxygen and organic biradicals.
4. Metals: The electrons in a metal are considered to be free like molecules in a gas. They tend to pair up but there are always a few unpaired electrons to produce a weak temperature independent paramagnetism known as pauli paramagnetism.

Langevin's classical theory of paramagnetism:

As has been pointed out above that the paramagnetic susceptibility is the magnetic analogue of the electrical orientational polarizability, therefore, a similar treatment may be used to calculate this. The following are the points of similarity in the two cases:

(i) There is an assembly of permanent dipoles independent of each other oriented randomly in the absence of an external field.

(ii) The potential energy of the dipoles have the same form:

$$U(\text{electrical}) = -P.E, \text{ and } U(\text{magnetic}) = -\mu_m.B$$

Thus, substituting μ_{in} for P and B for E, we can use the same Langevin-Debye theory to calculate the magnetization M which is given by

$$M = N\mu_m L(x) \qquad \ldots (34)$$

where $x \equiv \frac{\mu_{in}B}{kT}$ and the Langevin function $L(x)$ is:

$$L(x) = \coth x - \frac{1}{x}$$

For $x << 1$, $L(x) \equiv \frac{x}{3}$ as before, so that $M = \frac{N\mu_{in}^2 B}{3kT}$

$$\Rightarrow \qquad \chi = \frac{M}{H} = \frac{\mu_0 N\mu_m^2}{3kT} = \frac{C}{T} \qquad \ldots (35)$$

where $C = \frac{\mu_0 N\mu_m^2}{3k}$ is known as Curie constant. Consequently equation (35) is known as Curie law. The susceptibility versus temperature curve is shown in figure.

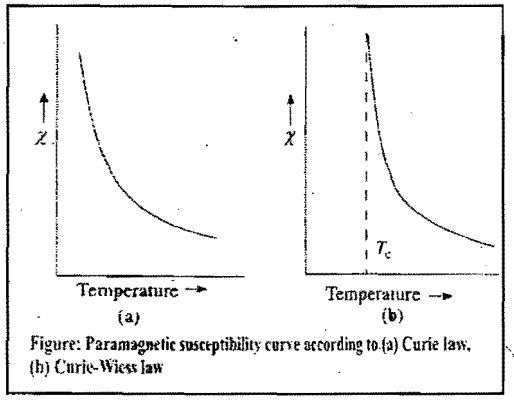


Figure: Paramagnetic susceptibility curve according to (a) Curie law, (b) Curie-Wiess law

Example: Approximately how large must be the magnetic induction for the orientation energy to be comparable to the thermal energy at room temperature? Assume $\mu_m = 5\mu_B$.

Soln. Given: $\mu_B = 5\beta_B$, $T = 300K$, $B = ?$

Here, the magnetic energy $= \mu_{in}B$ and the thermal energy kT. Now according to the question $\mu_{in}B = kT$

$$\Rightarrow \qquad B = \frac{kT}{\mu_B} = \frac{kT}{5\mu_B} = \frac{1.38\times10^{-23}\times300}{5\times9.27\times10^{-24}} = 89.32 \text{ W/m}^2 \simeq 10^2 \text{ W/m}^2$$

Example: Given: $N = 10^{28}$ ions$/m^3$, $\mu_m = \mu_B = 9.27\times10^{-24}$ A/m^2, $H = 10^6$ A/m,

We know that the paramagnetic susceptibility is given by

$$\chi = \frac{\mu_0 N \mu_m^2}{3kT} = \frac{4\pi\times10^{-7}\times10^{28}\times\left(9.27\times10^{-24}\right)^2}{3\times1.38\times10^{-23}\times300} = 0.87\times10^{-4}$$

Further, the magnetization is given by

$$M = \chi H = 0.87\times10^{-4}\times10^6 = 87 \text{ A/m}$$

Fundamentals of quantum theory of paramagnetism:

The Langevin's classical theory of paramagnetism is incapable of providing a consistent explanation of the magnetic phenomena resulting from the motion of electric charges. The very basis of the classical theory that all orientations of magnetic moments with respect to B are possible, is wrong according to quantum considerations. To overcome various difficulties, let us discuss the essence of quantum theory of paramagnetism based on the following basis facts:

1. For each unit of orbital angular momentum, an electron in an atom has one Bohr magneton $(\mu_B = eh/4\pi m)$ of magnetic moment associated with it. The magnetic moment is antiparallel to the angular momentum.
2. For each unit of spin angular momentum $(\hbar/2)$, there is also associated one half Bohr magneton $(\mu_B/2)$ of magnetic moment to an electron.
3. The total effective angular momentum of an electron is described as the vector sum of orbital and spin contributions, i.e.
   $$J = L + S \qquad \ldots(36)$$
4. The effective magnetic moment is given by
5. According to quantum mechanics, the magnitude of the angular momentum vector is given by $\{J(J+1)\}^{1/2}$ and not by simply J. Also there are 2J + 1 ways in which the atomic dipoles may orient relative to the magnetic field. The probability of such orientation is determined by the Boltzmann factor $\exp(-\Delta U/kT)$.

For simplicity, let us consider the atoms with L = 0. This gives g = 2, and J = S = 1/2 which in turn provide only two possible states. The lower level $(m_s = m_l = -1/2)$ corresponds to the moment parallel to the field, while the upper level corresponds to the moment opposite to the field.

Let N_1 and N_2 be the concentration of atoms in the lower and upper levels, respectively and that $N_1 + N_2 = N$ the total number of atoms. The difference of these concentrations produces a magnetization.

$$M = g\mu_B(N_1 - N_2) \qquad \ldots(37)$$

where $g\mu_B$ is the z-component of the magnetic moment when it is fully aligned with the field. These two concentrations are related by the expression.

$$\frac{N_1}{N_2} = \frac{\exp(+\Delta U/kT)}{\exp(-\Delta U/kT)} \qquad \ldots(38)$$

where $\Delta U = g\mu_B B$. Now assuming $x = g\mu_B B/kT$, we obtain

$$N_1 - N_2 = N\left(\frac{e^x - e^{-x}}{e^x + e^{-x}}\right) = N\tanh(x)$$

So, that $M = g\mu_B(N_1 - N_2) = Ng\mu_B\tanh(x)$ ...(39)

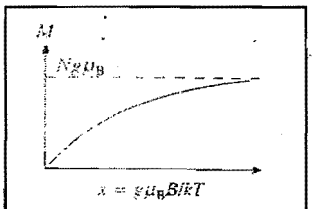


Figure: Magnetization M versus x for a system with J = 1/2

Figure shows a curve between the magnetization M and $x = g\mu_B B/kT$. At low field, M is proportional to B, but at higher fields M begins to saturate and eventually reaches a maximum value $Ng\mu_B$ when all the dipoles turn parallel to the field. Thus, for low field $x << 1$, and hence $\tanh(x) \sim x$, so that equation (39) becomes

$$M = Ng\mu_B x = \frac{N(g\mu_B)^2 B}{kT} = \frac{\mu_0 N(g\mu_B)^2 H}{kT} \qquad ...:(40)$$

Therefore, the paramagnetic susceptibility is given by

$$\chi = \frac{M}{H} = \frac{\mu_0 N(g\mu_B)^2}{kT} \qquad ... (41)$$

Now, in a magnetic field, for a system of atoms with L = 0 and J = S = 1/2, the projection of magnetic moment is similar to that the spin momentum. In equation (41), μ_B is projected value of moment whereas the magnitude of the effective moment of the atom is given by

$$\mu_{eff} = 2g\mu_B \{J(J+1)\}^{1/2} = \sqrt{3}\, g\mu_B \qquad \text{for} \qquad S = J = \frac{1}{2}$$

$$\Rightarrow \qquad \mu_{eff}^2 = 3g^2\mu_B^2 \quad \Rightarrow \quad g^2\mu_B^2 = \frac{\mu_{eff}^2}{3} \qquad ... (42)$$

Substituting this in equation (41), we have

$$\chi = \frac{\mu_0 N \mu_{eff}^2}{3kT} \qquad ... (43)$$

which is in agreement with the classical result. However, for J > 1/2 an atom with angular momentum quantum number J has $(2J+1)$ equally spaced energy levels. The magnetization is then given by

$$M = N_g J\mu_B B_J(x), \text{ with } x \equiv \frac{gJ\mu_B B}{kT} \qquad ... (44)$$

where the Brillouin function B_J is defined as

$$B_J(x) = \frac{(2J+1)}{2J}\coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right) \qquad ... (45)$$

where J becomes very large, the Brillouin function becomes identical to the Langevin function, i.e.

$$L(x) = \coth x - \frac{1}{x} \equiv \frac{x}{3} \qquad ... (46)$$

Therefore, from equation (43), the susceptibility becomes

$$\chi = \frac{\mu_0 NJ(J+1)g^2\mu_B^2}{3kT} = \frac{\mu_0 Np^2\mu_B^2}{3kT} = \frac{\mu_0 N\mu_{eff}^2}{3kT} \qquad \ldots(47)$$

where the effective moment of the atom, is now defined as $\mu_{eff} = p\mu_B$ and $p = g\{J+1\}^{1/2}$ is called the effective number of Bohr magneton for the atom.

Paramagnetism of free electrons:

According to Langevin's theory (equation 38), the paramagnetic susceptibility is inversely proportional to the temperature. However, some metals have been found to exhibit paramagnetism independent of temperature. It was W. Pauli (1927) who demonstrated that this is due to paramagnetism of free electrons (that constitute the electron gas), since they can orient only in two directions, either along the manetic field or against it.

In order to understand the existence of Pauli paramagnetism, let us recall the curve between density of states versus energy (figure) at absolute zero of temperature. That curve may be split into two parts with spins pointing in the +ve z-direction and other with spin in the opposite direction, as shown in figure . IN the absence of an external electric field, the distribution of electrons with spins parallel to z-direction, the energy of the spins aligned parallel to B is lowered by the amount μ_B, while the energy of the spins opposite to B is raised by the same amount (figure). As a result of this, the Fermi level for the two spin distribution shift with respect to each other and give to rise to energetically unstable situation. In order to acquire the stable configuration, the electrons lying near the Fermi level with antiparallel spins flip into the region of parallel spins until the two Fermi levels become equal again. (Figure).

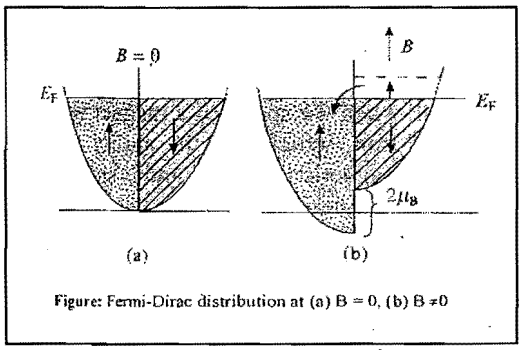


Figure: Fermi-Dirac distribution at (a) B = 0, (b) B ≠0

The number of electrons which effectively change their directions is equal to the density of states at the energy level in one of the spin distribution times the change in energy, i.e.

$$N_{eff} = \frac{1}{2}g(E_F)\mu_B B \qquad \ldots(48)$$

where the factor 1/2 is due to the fact that the density of states of one spin distribution is half of the total density of states. Thus after the application of the field, the number of electrons with spins parallel to the field is greater than the electrons with opposite spin by N_{eff}, leading to a net magnetization. Since the each flip increases the magnetization by $2\mu_B$ (from $-\mu_B$ to $+\mu_B$), the net magnetization is given by

$$M = N_{eff} \times 2\mu_B = g(E_F)\mu_B^2 B \qquad \ldots(49)$$

and hence the Pauli spin susceptibility of the electron gas is:

$$\chi_p = \mu_0\mu_B^2 g(E_F) \qquad \ldots(50)$$

According to equation (50), χ_p is essentially temperature independent. This is clear from the fact that temperature has a very small effect on the Fermi-Dirac distribution of the electrons.

$$g(E_F) = \frac{3N}{2E_F}$$

So, that, $$\chi_p = \frac{3\mu_0 N\mu_B^2}{2E_F} = \frac{3\mu_0 N\mu_B^2}{2kT_F} \quad \ldots(51)$$

where $E_F = kT_F$. This equation can be rewritten in terms of the classical susceptibility as

$$\chi_p = \frac{3}{2}\chi\frac{T}{T_F} \quad \ldots(52)$$

where $\chi = \frac{\mu_0 N\mu_B^2}{kT}$ for J = 1/2. Since, T_F is normally very high, χ_p is smaller than χ by about two orders of magnitude, which is in agreement with the experimental results. In transition metals, the paramagnetic susceptibility, χ_p is exceptionally high, because $g(E_F)$ is large.

Ferromagnetism:

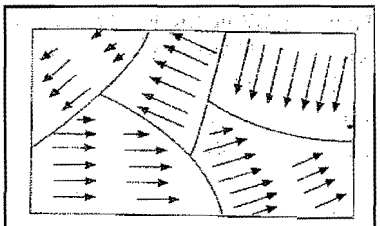


Figure: Ferromagnetic domain

In general, when we speak of a magnet we actually mean a ferromagnet. For example, consider a piece of iron, which has the ability to pick up other pieces of iron towards it, possesses permanent magnetic moments and is said to be a permanent magnet. Thus, ferromagnetism is the existence of magnetization even in th absence of the external magnetic field. Phenomenonlogically, it is the magnetic analogue of ferroelectricity. Some of the experimentally observed facts are:

1. Magnetization M increases when an external field is applied to the specimen. Moreover, the relationship between magnetization M and applied field H is nonlinear and shows hysteresis effect similar to that shown by polarization P and the electric field E.
2. The strong magnetism is found to disappear at a critical temperature (Tc), the specimen becomes demagnetized, behaves like a paramagnet and shows magnetic effects only when an external field is applied.
3. Ferromagnetic materials are made up of large number of 'domains' (each domain contains about $10^9 - 10^{15}$ atoms), which are spontaneously magnetized. The magnitude of spontaneous magnetization (referse to a single domain) of the specimen is determined by the vector sum of the magnetic moments of the individual domains (Figure).
4. Within a given domain, all the dipoles (spins) are aligned in the same direction, so that magnetization is the maximum possible value for a given material and temperature.

The weiss molecular (Exchange) field:

In order to explain the spontaneous magnetization of a ferromagnetic material, Weiss (1907) assumed that there exists an internal molecular field (also called exchange field H_{ex}) acting on a given dipole and is given by

$$H_{ex} = H + \lambda M \quad \ldots(53)$$

where λ is called Weiss constant (it is independent of temperature) and H is applied field. In a ferromagnet the

Curie law holds for exchange field as well. Therefore,

$$\frac{M}{H_{ex}} = \frac{C}{T} \qquad \ldots (54)$$

Simplifying the equation (53) and (54), we have

$$M = \frac{CH}{T - C\lambda} \qquad \ldots (55)$$

Therefore, the ferromagnetic susceptibility becomes,

$$\chi = \frac{M}{H} = \frac{C}{T - C\lambda} = \frac{C}{T - T_c} \qquad \ldots (56)$$

where $T_c = C\lambda$ is called the Curie temperature and the equation (56) is known as Curie-Weiss law. The coresponding variation of suscepbitibility with temperature is shown in figure. As long as $T \geq T_c$, this curve and the curve shown in figure are similar. However, as $T \to T_c$. Curive Weiss susceptibility tends to infinity and for $T \leq T_c$ there exists a spontaneous magnetization in the material even in the absence of an external field.

Temperature dependence of spontaneous magnetization:

As discussed above, the magnetic moments due to the orbital motion of free electrons in a metal is negligible in comparision to the spin moments. Therefore, assuming only the spin system, it is possible to determine the magnetic behaviour of a ferromagnetic material below the Curie temperature. In the absence of an external field ($H = 0$), equation (53) reudce to

$$H_{ex} = \lambda M \qquad \ldots (57)$$

where $M = N\bar{\mu}$ is the spontaneous magnetization at some temperature T less than T_c.

According to quantum theory of paramagnetism, the magnetization M for spin half ($S = J = 1/2$) is given by

$$M = N_g \mu_B \tanh(x) \qquad \ldots (58)$$

where, $$x = g\mu_B B / kT \qquad \ldots (59)$$

For ferromagnetic case, we must replace the field B by H_{ex} given by equation (57). Therefore,

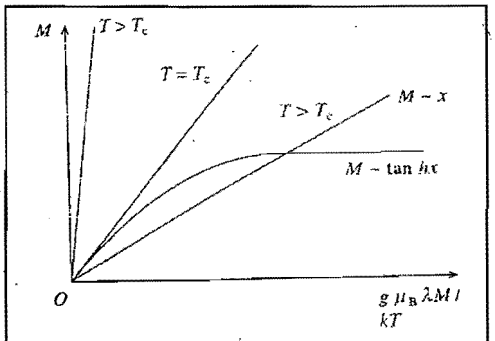


Figure: M versus x and M versus tan hx curves. The point of intersection represents spontaneous magnetization

$$x = \frac{\mu_0 g \mu_B \lambda M}{kT} \quad \Rightarrow \quad M = \frac{kT}{\mu_0 g \mu_B \lambda} x \qquad \ldots (60)$$

The equation (58) and (60) can be solved simultaenously by plotting them on M versus x graph. The value of M at a given temperature is obtained from the point of inersection of the two curves. It is clear that if T increases, the slope of the straight line also increases. For temperatures below a critical value $(T < T_c)$, the two curves intersect at a point, which gives a non vanishing spontaneous magnetization. The maximum spontaneous magnetization occurs at T = 0K and is given by

$$M_s(0) = Ng\mu_B \qquad \ldots(61)$$

At $T = T_c$ the straight line is tangential to the hyperbolic curve (equation ()) at the origin where the sponteaneous magnetization just reduces to zero and remains zero for all temperatues above the critical value $(T > T_c)$.

Further, at $T = T_c$, for $x << 1$, the hyperbolic function can be approximated as

$$\tanh(x) = x$$

Now we have, $$\lambda = \frac{kT_c}{\mu_0 N(g\mu_B)^2} \qquad \ldots(62)$$

In order to describe the temperature dependence of spontaneous magnetization in a convenient manner,

$$\frac{M_s(T)}{M_s(0)} = \tanh\left(\frac{T}{T_c}\right) \qquad \ldots(63)$$

This expresses the relation between the normalized magnetization $M_s(T)/M_s(0)$ and normalized temperature T/T_c. This is called thermomagnetic equation of state for the ferromagnetic phase of materials and is shown in figure (For Ni and Gd with J = 1/2 and 7/2). This curve is universal in the sense that the ferromagnetic materials for same J value. At 0K, the magnetization is at a maximum and the normalized magnetization $M_s(T)/M_s(0)$ is unity. As the temperature is increased, thermal energy randomizes the system. As a result, the spontaneous magnetization ceases to exist above Curie temperature. This behaviour is quite similar to order-disorder transition in binary alloys in which an ordered array of atoms at low temperature, gradually loses its orderedness with increasing temperature and eventually becomes completely disorderd at the transition temperature.

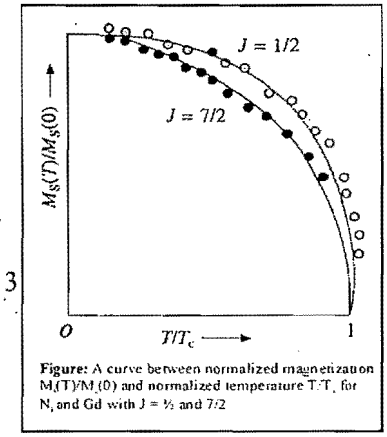
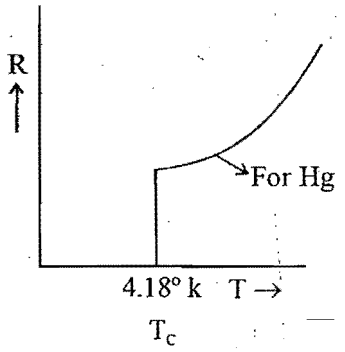


Figure: A curve between normalized magnetizaion $M_s(T)/M_s(0)$ and normalized temperature T/T_c for Ni and Gd with J = ½ and 7/2

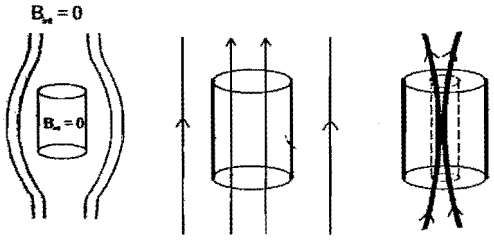
Chapter-8: SUPERCONDUCTIVITY

In 1911 Kammerling onnes discovered that the electrical resistance of Hg (mercury) at low temperature $\simeq 4.18$ k, vanishes (zero) suddenly. This phenomenon was given the name superconductivity. The temperature at which the resistance disappear (in zero mag. field) is called the transition temperature or critical temperature (T_c). The transition temperature of mercury is 4.18 °k, materials which shows this phenomenon are called superconducters.



Meissner's effect:

This effect is useful to make difference between superconductor and perfect (normal) conductor. When a superconductor and a perfect conductor are placed in an external magnetic field, the mag. line of the forces do not passes through the superconductor and they are swept away. Thus making the mag. field (B) inside the superconductor equal to zero. While line of mag. force passes through the perfect conductor and therefore B is not equal to zero inside the perfect conductor.



As in case of superconductor mag. field $B = 0$

$\Rightarrow \quad \mu_0(H+I) = 0$ [M.K.S unit] In C.G. S. $\vec{B} = \vec{H} + 4\pi I$

$\Rightarrow \quad H + I = 0 \quad \Rightarrow \quad \frac{I}{H} = -\frac{1}{4\pi} \quad \Rightarrow \quad \frac{I}{H} = -1 \quad \Rightarrow \quad \boxed{\chi = -1}$

Where χ = succeptibility, H = Magnetic field intensity and I is magnetization.

Thus the succeptibility of a super conductor is –ive which implies that a superconductor exhibits the properties of perfect diamagnetic susbtances.

Isotope effect:

It has been found that the critical temperature (T_c) of superconductor is found to be proportional to the negative half power of isotopic mass of the element i.e.

$T_C \propto M^{-1/2}$ $\qquad \boxed{M^{1/2}T_C = \text{constant}} \qquad \ldots (1)$

In mercury T_c varies from 4.185°k to 4.146 k as the isotopic mass (M) varies from 199.5 a.m.u. to 203.4 a.m.u. The debye temperature (θ_D) of phonon spectrum is also proportional to $M^{-1/2}$, so that

$\theta_D \propto M^{-1/2} \quad \Rightarrow \quad \theta_D M^{1/2} = \text{constant} \quad \ldots (2)$

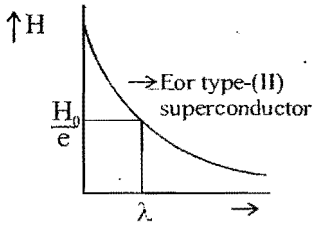
Eq^n.(1) divided by eq^n. (2) gives

$$\boxed{\frac{T_C}{\theta_D} = \text{constant}}$$

Persistent current:

In the super conductors current contineously flows as long as the material is kept below the critical (Transition) temperature (T_c). Since the current is very high and the decay formula is $i = i_0 e^{-(R/L)t}$. So once started it continue to flow indenfinitely as long as the temperature and magnetic field remain unchanged. This is called the persistent current.

The magnetic field and surface current penetrate in a superconductor to a depth of 10–100 nanaometer.



$$H = H_0 e^{-x/\lambda}$$

Similarly, $J_s = J_0 e^{-x/\lambda}$

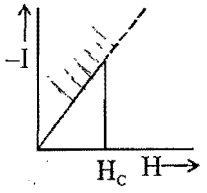
λ = penetration depth

Type-I and type-II sperconductors:

Super conductors are classified into the two parts

(i) Soft (type-1) superconductor (ii) Hard (type-II) superconductors

(i) Type-I superconductors: "Superconductor which exhibits complete meissner effect i.e. they are completely diamagnetic are called type-I or soft superconductors". The magnetization curve for type-I superconductor is shown in fig.1. below. It is disappointing that the critical mag. fields of superconductors are very low. Since the super current are started, continuously flow without heat loss. It was thought that mag. field could be produced and current is maintained without anly loss of energy. This is true, but if the mag. field produced exceed H_c, the material goes normal and current cannot be maintained by it. This was noted in 1916 by silsbee and is known as silsbee effect.



[Fig.1.]

(ii) Type-II superconductors:

These superconductors behaves differently as shown in fig.2. For applied field below H_{C1}, the material is diamagnetism and hence the field is H_{C1} is called the lower critical field. Above H_{C1} magnetic flux begins to enter in the superconductor upto an upper critical field H_{C2} at which superconductivity disappear. The magnetization curve for type-II superconductor is shown in fig.2a. The magnetic phase diagram for these super conductor is shown in fig.2b.

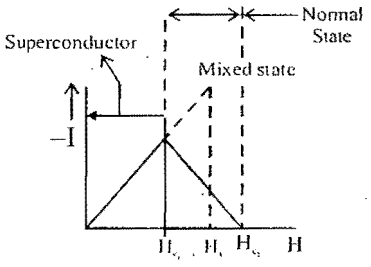
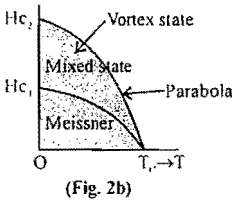


Fig. 2a

$$H_C = \sqrt{H_{C_1} \times H_{C_2}}$$



(Fig. 2b)

Properties which change in the superconducting transition:

(i) All the thermo electric effects disappear in the superconducting state.

(ii) The specific heat changes discontinuously at the transition temperature in the pressure of magnetic field.

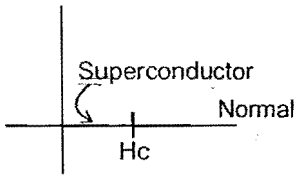
(iii) There is also a small change in volume, in presence of magnetic field.

(iv) The thermal conductivity changes discontinuously when superconductivity is destroyed in a magnetic field.

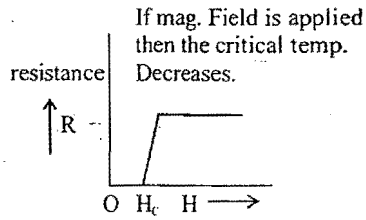
• Critical magnetic field:

If a magnetic field is applied parallel to the length of the superconducting wire, the resistance of the wire is suddenly restored at definite magnetic field, which is a function of the temperature and is characteristic of particular metal. This field is known as the critical field magnetic field (H_C). The critical magnetic field H_C is given by the relation

$$H_C = H_{C0}\left[1-\left(\frac{T}{T_C}\right)^2\right]$$



Where H_C = critical magnetic field at absolute zero.



• Penetration depth (λ):

'London' described the Meissner effect (B=0) and zero resistivity case of superconductors. He added E = 0 for zero resistivity.

$$\text{As}\left(J=\sigma E \;\&\; E=\frac{J}{\sigma}=\frac{I}{\infty}=0\right)$$

B= 0 according to Meissner effect.

As we know that, $\bar{\nabla}\times\bar{E}=-\frac{\partial\bar{B}}{\partial t}$

But $E=0 \Rightarrow 0=\frac{-\partial\bar{B}}{\partial t} \therefore \Rightarrow \bar{B}\neq 0$

Then London suggested that applied external magnetic field does not suddenly drop to zero at the surface of superconductor but decays exponentially according to the equation.

$$H = H_0 e^{-x/\lambda}$$

where H_0 = magnetic field intensity at the surface of the superconductor.

λ = Characteristic length (known as the penetration depth) at which H falls from H_0 to H_0/e.

• London equation:

According to the London theory, it is assumed that there are two types of conduction e^{-s} in a superconductor, namely, the super and the normal e^-'s. At 0 K a superconductor contains only super e^{-s} but as the temperature increases the number of normal e^-'s increases and above the transition temperature (T_C) all the e^{-s} are normal.

Let n_n, v_n and n_s, v_s is the e^-'s density, velocity in normal and superconducting state respectively. Then the average carrier density $(n) = n_n + n_s$

The current density $\bar{J} = \bar{J}_n + \bar{J}_s = e\,n_n\bar{v}_n + en_s\bar{v}_s$ ... (1)

For the superconducting e^-'s.

$$m\frac{d\bar{V}_s}{dt} = e\bar{E} \Rightarrow \frac{d\bar{V}_s}{dt} = \frac{e\bar{E}}{m} \qquad \left[\text{as } \bar{F} = m\bar{a} = m\frac{d\bar{V}}{dt} = e\bar{E}\right]$$

and $\bar{J}_s = en_s\bar{V}_s \Rightarrow \quad \frac{d\bar{J}s}{dt} = e\,n_s\left(\frac{e\bar{E}}{m}\right)$

$$\Rightarrow \quad \boxed{\frac{d\bar{J}_s}{dt} = \frac{n_s\, e^2\bar{E}}{m}} \qquad \ldots(2)$$

equation (2) is known as the first london equation and it describes the absence of resistance.

If $\bar{E} = 0$

$$\Rightarrow \quad \frac{d\bar{J}_s}{dt} = 0 \quad \Rightarrow \quad \bar{J}_s = \text{const.}$$

Then it becomes possible to have steady (constant) current in the absence of electric field. This is the superconducting phenomenon.

The corresponding equation for the normal current is:

$$\boxed{\bar{J}_n = \sigma_n\bar{E} = \frac{n_n e^2\tau\,\bar{E}}{m}} \qquad \ldots(3)$$

This equation shows that an electric field is necessary for establishing a steady current in normal metal. If $\bar{E} = 0$, $\bar{J}_n$ becomes zero.

Now by the Maxwell's equation.

$$\bar{\nabla}\times\bar{E} = -\frac{\partial\bar{B}}{\partial t} \quad \Rightarrow \quad \bar{\nabla}\times\bar{E} = -\mu_0\frac{\partial\bar{H}}{\partial t} \qquad \ldots(4)$$

Now taking curl of equation (2), we get

$$\bar{\nabla}\times\frac{d\bar{J}_s}{dt} = \frac{n_s\, e^2\left(\bar{\nabla}\times\bar{E}\right)}{m}$$

$$\frac{\partial}{\partial t}\left(\bar{\nabla}\times\bar{J}_s\right) = \frac{n_s e^2}{m}\left(-\mu_0\frac{\partial H}{\partial t}\right) = -\frac{\mu_0 n_s\, e^2}{m}\frac{\partial H}{\partial t} \qquad \ldots(5)$$

Integrating this equation, we get $\boxed{\bar{\nabla}\times\bar{J}_s \equiv -\frac{n_s\, e^2\mu_0\,\bar{H}}{m}}$ ...(6)

Equation (6) is second London equation and explains meissner effect $\left(\text{i.e. } \bar{H} = 0 \Rightarrow J_s = \text{constant}\right)$

- **Calculation of penetration depth:**

Taking curl of equation (6) we get

$$\bar{\nabla}\times\left(\bar{\nabla}\times\bar{J}_s\right) = -\frac{n_s\, e^2\,\mu_0}{m}\left(\bar{\nabla}\times\bar{H}\right)$$

Or, $\quad \bar{\nabla}\left(\bar{\nabla}.\bar{J}_s\right) - \left(\bar{\nabla}.\bar{\nabla}\right)\bar{J}s = -\frac{n_s\, e^2\,\mu_0}{m}\left(\nabla\times H\right)$ (as $\bar{J}s = \text{constant}$)

$$\Rightarrow \quad \nabla^2 \bar{J}s = \frac{\mu_0 n_s e^2}{m}\left(\bar{\nabla} \times \bar{H}\right) \qquad \ldots (7)$$

But $\quad \bar{\nabla} \times \bar{H} = \bar{J} + \frac{\partial \bar{D}}{\partial t} = \bar{J}_n + \bar{J}_s + \frac{\partial \bar{D}}{\partial T}$

where $\bar{D}$ is the electric displacement vector. For direct current case we can neglect $\bar{J}_n$ and $\frac{\partial \bar{D}}{\partial t}$, so that

$\bar{\nabla} \times \bar{H} = \bar{J}_s$

$\therefore$ equation (7) becomes $\quad \nabla^2 \bar{J}s = \frac{\mu_0 n_s e^2}{m} \bar{J}_s = \frac{\bar{J}_s}{\lambda^2} \qquad \ldots (8)$

where $\boxed{\lambda^2 = \frac{m}{\mu_0 n_s e^2}} \qquad \ldots (9)$

λ has the dimension of length and is called the penetration depth.
The solution of equation (8) is

$$\boxed{J_s = A\, e^{x/\lambda} + Be^{-x/\lambda}} \qquad \ldots (10)$$

The first factor of this equation shows that J_s increases as x increases which is contrary to the fact. Then it can be left.

$\therefore$ equation (10) gives $\quad J_s = B\, e^{-x/\lambda}$

at $\quad x = 0 \quad J_s = J_0 \Rightarrow B = J_0$

$$\Rightarrow \quad \boxed{J_s = J_0 e^{x/\lambda}} \qquad \ldots (11)$$

at $\quad x = \lambda, J_s = J_0/e$

Thus λ (penetration depth) is the distance in the superconductor at which the current value falls to 1/e of its value at the surface.

- **Drawback of London theory:**

Though the London theory explains the two conditions E = 0, B = 0 characterising the superconducting state but it does not tell us about the process happening inside the superconductors The process which takes place inside the superconductors is explained by BCS theory.

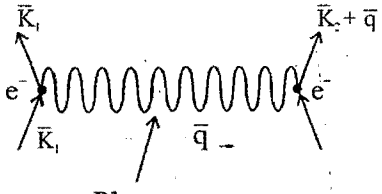
- **BCS Theory: [Bardeen, Cooper Schrieffer theory):**

This theory explains the microscopic phenomenon which takes place inside the super cnductor. It give, the better explanation of the superconductivity then any other theory. This theory involves the following four steps.

(i) Electron-lattice - electron interaction:

When an e^- come in contact to the lattice it deforms the lattice and at the same time another e^- come in contact to the deformed lattice to take the advantage of lattice deformation. In turns of it the lattice also applied a force on these e^{-s}. Thus there is an interaction between e^- & e^- in which the phonon (lattice vibration) acts as a mediator.

(ii) **Cooper pair:** The fundamental postulate of BCS theory is that superconductivity phenomenon occurs, when the attractive interaction between two e^{-s} by means of a phonon exchange dominates the usual repulsive coulomb interaction. Two such e^{-s} which interact attractively in the phonon field are called a cooper pair. These cooper pair behave like a single particle. The energy of the pair of e^{-s} in the pound state is less than the energy of the pair in free state (e^- seperated). The difference of the energy of the cooper pair and that of the energy of the cooper pair and that of free e^{-s} is equal to the binding energy of the cooper pair. At temperature less than T_c e^-=lattice-e^- interaction is stronger than $e^- - e^-$ coulomb repulsion. Pairing is complete at T = 0° k and is completely broken at $T = T_c$.



Phonon

[**Fig.** e^-–e^- interaction through lattice phonon)

(iii) Existance of Energy gap:

The energy difference between the free state of e^{-s} and the paired state appears as the energy gap at the Fermi surface. The gap is max. at absolute zero temp. and becomes zero at $T = T_C$.

(iv) The paired e^{-s} [cooper pair] are not scattered because of their special property of smooth riding over the lattice imperfection without exchanging of energy with them. As a result of it they travel a certain distance in the coupled motion. This distance is called coherence length. It is of the order of 10^{-4} cm. Coherence length

$$(\xi_o) = \frac{\hbar V_F}{\pi E_g}; \quad V_F = \text{Velocity at Fermisurface}.$$

Expression for coherence length:

The London penetration depth λ_L is a fundamental length that characterized a superconductor. Another independent length of equal importance is the coherence length .....

Now the modulated wavefunction corresponding to wave function

$$\psi = e^{+ikx} \text{ is } \phi = \frac{1}{\sqrt{2}}\left[e^{i(k+q)x} + e^{ikx}\right] \quad ..(1)$$

Now the probability density corresponding to ϕ is:

$$\phi^*\phi = \frac{1}{\sqrt{2}}\left[e^{-i(k+q)x} + e^{-ikx}\right].\frac{1}{\sqrt{2}}\left[e^{i(k+q)x} + e^{ikx}\right]$$

$$= \frac{1}{2}\left[1+1+e^{-iqx} + e^{iqx}\right] = \frac{1}{2}\left[2 + 2\cos qx\right]$$

$$\Rightarrow \quad \phi^*\phi = \left[1+\cos qx\right] \quad ...(2)$$

The probability associted with the plane wave is

$$\psi^*\psi = e^{-kx}.e^{-ikx} = 1$$

The kinetic energy (E) of the wave function $\psi(x) = \frac{\hbar^2 k^2}{2m}$ ...(3)

While the K.E. for the modulated wave function ϕ is :

$$\int \varphi\left(\frac{\hat{p}z}{2m}\right)\varphi\, dx$$

$$\int \phi^*\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\phi\, dx = \int \frac{1}{\sqrt{2}}\left[e^{-i(k+q)x} + e^{-ikx}\right]\left(\frac{-\hbar^2}{2m}\right)\frac{d^2}{dx^2}\left[\frac{1}{\sqrt{2}}\left(e^{i(k+q)x} + e^{ikx}\right)\right]dx$$

$$= +\frac{\hbar^2}{4m}\int\left[e^{-i(k+q)x} + e^{-ikx}\right]\left[(k+q)^2 + k^2\right]\left[e^{i(k+q)} + e^{+ikx}\right]dx$$

$$= \frac{\hbar^2}{4m}\left[(k+q)^2 + k^2\right]\int\left[e^{-i(k+q)x} + e^{-ikx}\right].\left[e^{i(k+q)} + e^{ikx}\right]dx$$

$$= \frac{\hbar^2}{4m}\left[2k^2 + 2kq + q^2\right] \simeq \frac{\hbar^2}{2m}k^2 + \frac{\hbar^2}{2m}kq \qquad (\text{As } q << k)$$

Thus the increases in energy $= \frac{\hbar^2 kq}{2m}$ ... (4)

If this increase in energy exceeds the energy gap E_g, the superconductivity will be destroyed. The critical value of q_0 of the modulation vector is given by

$$\frac{\hbar^2 k_F q_0}{2m} = E_g \qquad \text{... (5)}$$

The intrinsic length (ξ_0) is defined as

$$\xi_0 = \frac{1}{q_0} = \frac{\hbar^2 k_F}{2mE_g} = \frac{\hbar P_F}{2mE_q} \Rightarrow \qquad \boxed{\xi_0 = \frac{\hbar V_F}{2E_g}}$$

By B.C.S theory $\boxed{\xi_0 = \frac{\hbar V_F}{\pi E_g}}$

$$\frac{\lambda}{\xi_0} = k$$

$k > \frac{1}{\sqrt{2}}$ For (Ist type superconductivity) and $< \frac{1}{\sqrt{2}}$ for IInd type superconductivity

- **Properties which do not change in superconductivity transitions:**

(i) There is no change in the reflectivity (Reflection coeff.) of the metal.
(ii) The X-ray diffraction pattern is same.
(iii) The photoelectric properties, remain unchanged.
(iv) The elastic properties do not change.
(v) In the atom of a mag. field there is no latent heat and hence no change in volume at the transition.

- **Super conductor band gap:** $E_g = 2.8\, k_B T_C$
- Cooper pair follow B.E. statistics. Its spin is zero.
- Super conductivity is of IInd order phase transition.

Main points of BCS theory of superconductivity:

The basis of a quantum theory of superconductivity was laid by the classic 1957 papers of Bardeen, Cooper and schrieffer. The BCS theory include.

(i) An attractive interaction between e^{-s} can lead to a ground state seperated from excited state by an energy gap. The critical field, the thermal properties and the most of the electromagnetic properties are consequencies of the energy gap.

(ii) The e^- -lattice-e^- interactin leads to an energy gap of the observed magnitude. The indirect interaction proceeds when one e^- interacts with the lattice and deforms it; a second e^- sees the deformed lattice and adjusts itself to take advantage of the deformation to lower its energy. Thus the second e^- interacts with the first e^- via the lattice deformation.

$e^- \sim\sim\sim\sim\sim\sim\sim\sim e^-$

(iii) The penetration depth of coherence length emerge as natural consequences of the BCS theory.

(iv) The criterion for the transition temperature T_c of an element or alloy involves the e–density of orbitals $D(E_F)$ at the Fermi level and the attractive e^--lattice - e^- interaction (U) and is given by

$$T_C = 1.14\,\theta_D \exp\left[-1/UD(E_F)\right]$$

(v) Magnetic flux through the superconducting ring is quantized and the effective unit of charge is 2e rather than e. $\phi = n\dfrac{h}{2e}, n = 1, 2, 3.....$ The BCS groundb state involves pairs of e^{-s}, having opposite wave vectors of opposite spins: $\bar{k}_1 = -\bar{k}_2$ & $S_1 = -S_2$. Such pairs of e^{-s} are called the cooper pairs.

Problem:

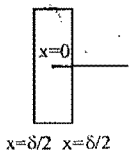
The penetration equation may be written as $\lambda^2\nabla^2 B = B$ where λ is the penetration depth. Show that $B(x)$ inside a superconducting plate perpendicular to the x axis and of thickness δ is given by

$$B(x) = B_a \frac{\cosh x/\lambda}{\cos h\,(\delta/2\lambda)}$$

Where B_a is the field outside the plate and parallel to it, and $x = 0$ is at the plate.

Soln. $\nabla^2 B = \dfrac{B}{\lambda^2}$

$\Rightarrow \quad B = Ae^{x/\lambda} + A'E^{-x/\lambda}$ ... (1)



Applying the condition

$B = B_a \mid x = \delta/2 \;\&\; x = -\delta/2$

$\Rightarrow \quad B_a = A\,e^{\delta/2\lambda} + A'e^{-\delta/2\lambda}$

Also, $B_a = Ae^{-\delta/2\lambda} + A'e^{\delta/2\lambda} \quad \Rightarrow \quad A = A'$ ... (2)

$\therefore \quad B_a = A\left(e^{\delta/2\lambda} + e^{-\delta/2\lambda}\right) = A\left(2\cosh \delta/2\lambda\right)$

$\Rightarrow \quad A = B_a/2\cosh \delta/2\lambda$ ... (3)

Putting (2) and (3) in (1), we get

$$B = B_a\left(\frac{\cosh x/\lambda}{\cosh \delta/2\lambda}\right)$$

• THERMODYNAMICS OF SUPERCONDUCTORS:

(i) Entropy in normal state is: $S_n = S_s - \mu_0\left[H_c \frac{dH_c}{dT}\right]$

At $T = T_C$ $\Rightarrow$ $\Delta S = S_n - S_s = 0$

$H_C = 0$ $\quad S_n = S_s$

Entropy of normal state ← ┘ └→ Entropy of superconducting state.

i.e. entropy is continuous at the transition point

(ii) Change in specific heat at T_C is:

$$\Delta_C = C_s - C_n = \mu_0 T_c\left(\frac{dH_c}{dT}\right)^2 \rightarrow \text{Rutger formula.}$$

$\Rightarrow$ $\Delta C \neq 0$; $\therefore$ Specific heat is discontinuous at the boundary.
at $T = T_C$.

Problem:

If $H_C = H_{C0}\left[1 - \frac{T^2}{T_C^2}\right]$ & $C_n = rT_c$,

Show that fractional charge in the heat capacity at the discontinuity is given by

$$\frac{C_s - C_n}{C_n} = \frac{4\mu_0 H_{C0}^2}{rT_C^2}$$

Soln. $$C_s - C_n = \mu_0 T_C\left(\frac{dH_C}{dT}\right)^2 \quad \ldots (1)$$

& $$H_C = H_{Co}\left[1 - \frac{T^2}{T_C^2}\right] \Rightarrow \frac{dH_C}{dT} = H_{Co}\left(0 - \frac{2T}{T_C^2}\right)$$

$$\Rightarrow \left(\frac{dH_c}{dT}\right)^2 = 4\frac{H_{Co}^2 T^2}{T_C^4} \quad \ldots (2)$$

Putting (2) in equation (1), we get

$$C_s - C_n = \frac{4\mu_0 H_{Co}^2 T^2}{T_c^3}$$

$$\therefore \quad \frac{C_s - C_n}{C_n} = \frac{C_s - C_n}{rT_c} = \frac{4\mu_0 H_{Co}^2 T^2}{rT_C^4}$$

At discontinuity $T = T_C$; $\frac{C_s - C_n}{C_n} = \frac{4\mu_0 H_{Co}^2 T_C^2}{rT_C^4}$

$$\Rightarrow \quad \boxed{\frac{C_s - C_n}{C_n} = \frac{4\mu_0 H_{Co}^2}{rT_C^2}}$$

JOSEPHSON SUPERCONDUCTOR TUNNELING:

There are many effects associated with the tunelling of superconducting e⁻-pairs from a superconductor through a layer of an insulator into another superconductor. Such a Juntion is called a weak link. Few such effects are

DC Josephson effect: A d.c. current flows across the juntion in the absence of any electric and magnetic field.

AC Josephson effect: A dc voltage applied across the junction causes rf current oscillations across the junction. This effect is utilized for precise measurement of $\hbar/e$. Further an rf voltage applied with d.c voltage can then cause a dc current

$$\omega = \frac{2eV}{\hbar}$$

PROBLEMS

Problem: Lead in the superconducting state has the critical temperature of 6.2 K at zero magnetic field and a critical field of 0.064 MAm–1 at 0 K. Determine the critical field at 4 K.

Ans. **0.037 MAm^{-1}.**

Problem: The transition temperature of mercury with an average atomic mass of 200.59 amu is 4.153 K. Determine the transition temperature of one of its isotopes, $_{80}Hg^{204}$

Ans. **4.11 K**

SUMMARY

1. A superconductor is characterized by two independent properties, viz, zero electrical resistance and perfect diamagnetism,
2. The phenomenon of flux exclusion in a superconductor is called the Meissner effect. It is independent of the history of superconductors and is reversible.
3. An applied magnetic field penetrates a superconductor up to a distance called the penetration depth. The resulting surface currents are known as supercurrents. The field penetration is quite small for T<Tc and is complete for T>Tc.
4. The superconducting state is stable only below a particular applied magnetic field called the critical field. This field decreases with increase in temperature so long as T<Tc and becoms zero when T equals Tc.
5. There exist two types of superconductors – type 1 or soft and type II or hard superconductors. Type I superconductors behave as perfect superconduters below a critical field H_C and as normal conductors above it. Type II superconductors have two critical fields, Hc_1 and Hc_2. Superconducting and normal states exist below and above the field Hc_1 and Hc_2 respectively whereas a vertex state exists in the range between Hc_1 and Hc_2.
6. The superconducting state is more ordered than the normal state. This order may extend up to a certain range called the coherence length.
7. Experiments on specific heat, infrared absorption and tunnelling suggest the existence of an energy agp which separates the superconducting electrons from the normal electrons.

8. The flux passing through the non-superconducting region of a superconducting ring is quntized; the quantum of flux is called a fluxoid and is equal to h/2e, where h is Planck's constant and e the electronic charge.

9. The BCS theory accounts for a superconducting state by considering coherence among the Cooper pairs. A Cooper pair is a pair of electrons having equal and opposite momenta and spins.

$$\lambda = \frac{\lambda_0}{\left[1-\left(\frac{T}{T_C}\right)^4\right]}$$

λ = Penetration depth at temperature T.

λ_0 = Penetration depth at temperature 0K.

Problems:

1. The critical temperature of a superconductor at zero magnetic field is Tc. Determine the temperature at which the critical field becomes half of its value at 0 K.

Ans. 0.707 Tc.

2. The critical fields at 6 K and 8 K for a NbTi alloy are 7.616 and 4.284 MAm–1 respectively. Determine the transition temperature and the critical field at 0 K.

Ans. 10 K, 11.9 MAm^{-1}.

3. Determine the frequency of the electromagnetic waves radiated by a Josephson junction across which a dc voltage of 0.5 mV is applied.

Ans. 2.14×10^{11} Hz.

4. The critical temperature T_C for Hg with isotopic mass 199.5 is 4.185 K. Calculate its critical temperature when its isotopic mass changes to 203.04. [**Hint:** $M^{1/2}T_C$ = constant]

Example: A superconductivity tin has a critical temperature of 3.7 k in zero magnetic field and a critical field of 0.0306 tesla at 0K. Find the critical field at 2K,

Soln. $$H_C = H_{CO}\left[1-\left(\frac{T}{T_C}\right)^2\right]$$

$$H_C = 0.0306\left[1-\left(\frac{2}{3.7}\right)^2\right] = 0.0231 \text{ Tesla}$$

Problem: For a specimen of V_3Ga, the critical fields are respectively 1.4×10^5 and 4.2×10^5 Ampere/metere for 14K and 13K. Calculate the transition temperature and critical fields at 0K and 402 K.

Soln. $$H_{C_1} = 1.4\times10^5 = H_{CO}\left[1-\left(\frac{14}{T_C}\right)^2\right] \quad \ldots(1)$$

$$H_{C_2} = 4.2\times10^5 = H_{CO}\left[1-\left(\frac{13}{T_C}\right)^2\right] \quad \ldots(2)$$

Solving these equations, we can find H_{CO} & T_C

Example: Estimate the intrinsics cohherence length of Al if energy gap $E_g = 3.4\times10^{-4}$ eV,

$V_F = 2.02\times10^{6}$ m/sec

Soln. Coherence length $\xi_0 = \dfrac{\hbar v_F}{\pi E_g} = \dfrac{1.05\times10^{-34}\times2.02\times10^{6}}{3.14\times3.4\times10^{-4}\times1.6\times10^{-19}}$

Example: What is the frequency of E.M.W. radiated by a Josephson function having a voltate of 650 μV across its terminals.

Soln. $\omega = \dfrac{2eV}{\hbar} \Rightarrow \upsilon = \dfrac{2eV}{h} = \dfrac{2\times1.6\times10^{-19}\times650\times10^{-6}}{6.6\times10^{-34}}$

Example: The London penetration depths for Pb at 3K and 7.1 K are respectively 39.6 nm and 137 nm. Calcualte its transition temperature and penetration depth at 0K.

Soln. $\lambda = \dfrac{\lambda_0}{\left[1-\left(\dfrac{T}{T_C}\right)^4\right]} \Rightarrow 39.6 = \dfrac{\lambda_0}{\left[1-\left(\dfrac{3}{T_C}\right)^4\right]}$

$$\text{Also } 137 = \frac{\lambda_0}{\left[1-\left(\dfrac{7.1}{T_C}\right)^4\right]}$$

Solving these we can obtain λ_0 and T_C.

Problem: Show that

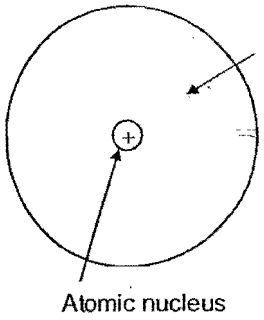
$$\underset{\text{entropy change}}{\Delta S} = S_n - S_s = \frac{2\mu_0 H_{C0}^2}{T_C}\left[\left(\frac{T}{T_C}\right)-\left(\frac{T}{T_C}\right)^3\right]$$

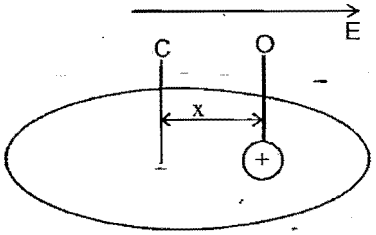
and $$\underset{\text{Sp. heat change}}{\Delta C} = C_n - C_s = \frac{2\mu_0 H_{C0}^2}{T_{C^2}}\left[\left(\frac{T}{T_C}\right)-3\left(\frac{T}{T_C}\right)^3\right]$$

[**Hint:** use $\Delta S = S_n - S_s = -\mu_0 H_C \dfrac{dH_c}{dT}$ and $\Delta C = C_n - C_s = -\mu_0 T_C \left[dH_C/dT\right]^2$

Chapter-9: DIELECTRICS

Electronic polarization : Displacemnt of electron on application of electric field.





$p_{induced} = \alpha E$ α = polarazibility

α_e = electronic polar.

$F_{restoring} = -\beta x$ and $z_{eE} = \beta x$.

$$p_e = (Ze)x = \left(\frac{z^2e^2}{\beta}\right)E$$

also $-\beta x = zm_e\frac{d^2x}{dt^2}$ $x(t) = x_o\cos(\omega_o t)$

Where $\omega_o = \left(\frac{\beta}{zm_e}\right)^{1/2}$ is the oscillation frequency of center of mass of the electron cloud.

x_0 = Displacemnet before the removal of field. After removal of the field charge cloud executes simple harmonic motion. Oscillation die out with time.

$$\alpha_e = \left(\frac{ze^2}{m_e\omega_0^2}\right)$$ (static electronic polarizability)

Polarization :

$P = X_e \epsilon_o E$ also $p = \alpha_e E$ and $P = Np_{induced} = N\alpha_e E$

$$\therefore X_e = \frac{N\alpha_e}{\epsilon_o}$$

Since, $\epsilon_r = 1 + X_e$ $\therefore \epsilon_r = 1 + \frac{N\alpha_e}{\epsilon_o}$

Claussius - Mossotti equation:

The induced polarization depends on the actual field experienced by the molecule.

Actual field depends not only on the applied field rather also depends on the orientation of the polarized molecule. (i.e., Polarization,)

$$E_{loc} = E + \frac{P}{3\epsilon_o}$$ and $P_{ind} = \alpha_e E_{loc}$

$$P = X_e \epsilon_o E = (\epsilon_r - 1)\epsilon_o E$$

$$P = NP_{ind} = N\alpha_e E_{loc} = N\alpha_e \left[E + \frac{P}{3\epsilon_o}\right]$$

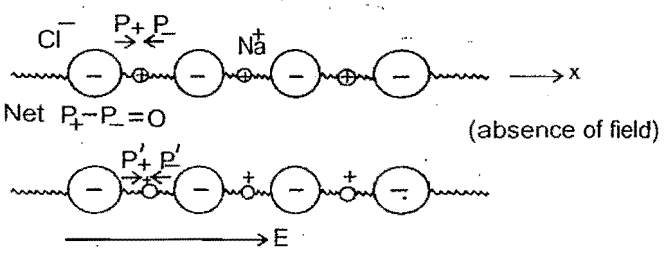
$$\Rightarrow P - \left(\frac{N\alpha_e}{3\epsilon_o}\right)P = N\alpha_e E \qquad \Rightarrow P\left(1 - \frac{N\alpha_e}{3\epsilon_o}\right) = N\alpha_e E \qquad \Rightarrow (\epsilon_r - 1)\epsilon_o \not{E}\left(1 - \frac{N\alpha_e}{3\epsilon_o}\right) = N\alpha_e \not{E}$$

$$\Rightarrow \frac{(\epsilon_r - 1)}{(\epsilon_r + 2)} = \frac{N\alpha_e}{3\epsilon_o}$$ Claussius Mossotti Eqn.

Polarization Mechanism:

(i) Ionic Polarization
(ii) Orientaticanl (Dipolar) Polarization } Total polarization
(ii) Interfacial

(i) Ionic Polarization:



P_+ Increases to P_+' and P_- decreases to P_-'

P_-' $P_{av} = P_+' - P_-'$ depends on the E. field.

$p_{av} = \alpha_i E_{loc}$ α_i = Ionic polarizabilty

$P = N_i p_{av} = N_i \alpha_i E_{loc}$

Ni = No. of ions per unit vol. and $P = (\epsilon_r - 1)\epsilon_o E$

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_o} N_i \alpha_i$$ claussius

electronic polarization just adds to it.

(ii) **Orientational Polarization:** - If dipole moment of one molecule = p_o then for N molecules per unit volume

$P = NP_o$.

Dipole energy in presence of E. field must be greater than thermal energy i.e, 5/2 kT

now $\tau = (F \sin\theta)a = Ep_o \sin\theta$

PE = 0 when $\theta = 0$, xax. PE when $\theta = 180°$

$$E_{max} = \int_0^{\pi} p_o E \sin\theta d\theta = 2p_o E$$

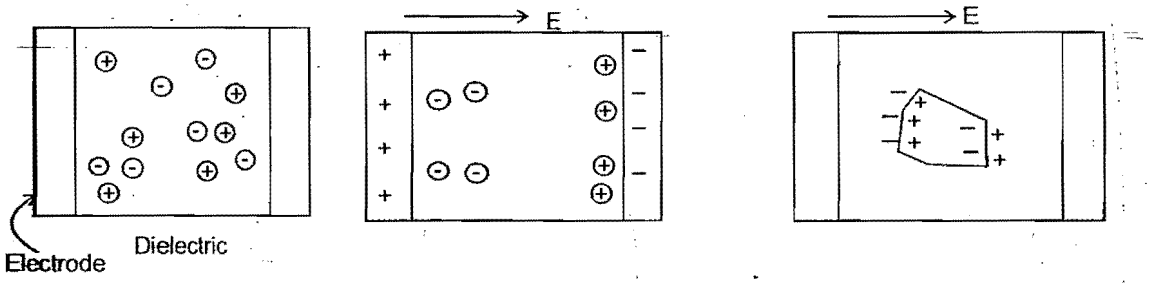
Avgerage value P_0E

p_{av} is proportional to the magnitude of p_o itself and also proportional to the ang. dipole energy to average thermal energy ratio . i.e.,

$p_{av} \propto p_o \frac{p_o E}{\frac{5}{2}kT}$ using Boltzmann statistics i.e $E \propto \exp(-E/kT)$

we get $p_{av} = \frac{p_0^2 E}{3kT}$ using local field $\alpha_d = \frac{p_0^2}{3kT}$ (Orientational polarizability inversely proportional to temp.)

(ii) Interfacial Polarization:



Total Polarization:

$p_{av} = \alpha_e E_{loc} + \alpha_i E_{loc} + \alpha_d E_{loc}$, $\boxed{\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{1}{3\epsilon_o}(N_e\alpha_e + N_i\alpha_i)}$

Example: Determine the percentage of ionic polarisibility in NaCl crystal which has optical index of refraction and the static dielectric constant as 1.5 and 5.6 respectively.

Soln. $\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N(\alpha_e + \alpha_i)}{3\epsilon_0}$

$\epsilon_r = 1.6 \qquad n = 1.5$

$$\frac{1.6-1}{1.6+2} = \frac{N(\alpha_e+\alpha_i)}{3\epsilon_0} \Rightarrow \frac{1}{6} = \frac{N(\alpha_e+\alpha_i)}{3\epsilon_0} \quad \ldots(1)$$

$$\frac{n^2-1}{n^2+2} = \frac{N\alpha_e}{3\epsilon_0} \Rightarrow \frac{2.25-1}{2.25+2} = \frac{N\alpha_e}{3\epsilon_0} \Rightarrow \frac{5}{17} = \frac{N\alpha_e}{3\epsilon_0} \quad \ldots(2)$$

(1) Divided by eqn. (2)

$$\frac{1}{6}\times\frac{17}{5} = \frac{N(\alpha_e+\alpha_i)}{3\epsilon_0}\times\frac{3\epsilon_0}{N\alpha_e} \Rightarrow \frac{17}{30} = 1+\frac{\alpha_i}{\alpha_e}$$

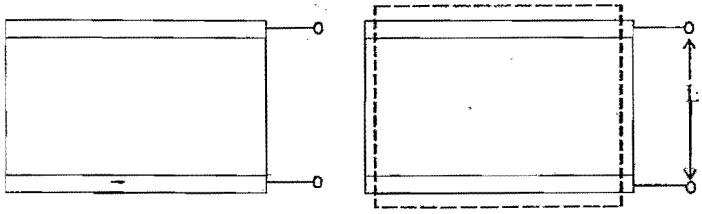
$$\frac{17}{30} - 1 = \frac{\alpha_i}{\alpha_e} \Rightarrow 1 - \frac{\alpha_e}{\alpha_e+\alpha_i} = \frac{30}{17}$$

$$\Rightarrow \boxed{\frac{\alpha_i}{\alpha_e+\alpha_i}\times 100 = \left[1-\left(\frac{n^2-1}{n^2+2}\right)\left(\frac{\epsilon_r+2}{\epsilon_r-1}\right)\right]\times 100}$$

$$= \left[1-\left[\frac{(1.5)^2-1}{(1.5)^2+2}\right]\left(\frac{5.6+2}{5.6-2}\right)\right]\times 100 = 51.4\%$$

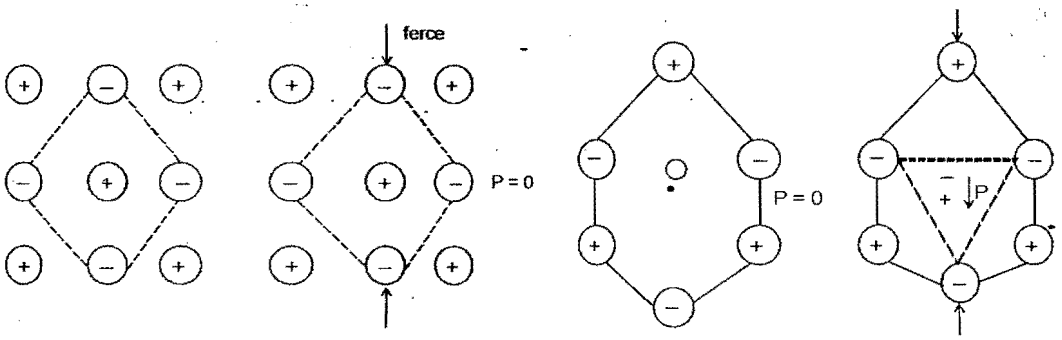
Piezoelectricity:

Certain Crystals eq. Quartz., (crystalline SiO_2) and $BaTiO_3$ becomes polarized when mechanically stressed, appearance of surface charge leads to voltage difference b/n the two surfaces of the Crystal.
Same Crystal also exhibit Mechanical strain or distortion when they experience electric field.



Only certain Crystal can exhibit that which has no centre of symmetry.
Eample NaCl type has centre of symmetry

Example: Hexagonal



Non centrosymmetric Direction of Polarization depends on the dirn of applied stress.
Generally an applied strees in one direction can give rise to induced polarization in other Crystal direction.
Suppose

T_j = applied Mechanical stress along some j direction
P_i = Induced Polarization along some i direction
Two are linearly related as

$P_i = d_{ij} T_j$
d_{ij} = piezoelectric coefficient.
The converse Piezoelectric effect is that b/w an induced strain S_j and j and an applied electric field E_i along i

$S_j = d_{ij} E_i$

They are called transducers because they convert electrical signal, electric field to mechanical signal, strain & vice versa used in microphones, Ultrasonic transducers.
Electromechanical coupling factor k.

$$k^{\Omega} = \frac{\text{Electrical energy converted to Mechanical energy}}{\text{Input of electrical energy}}$$

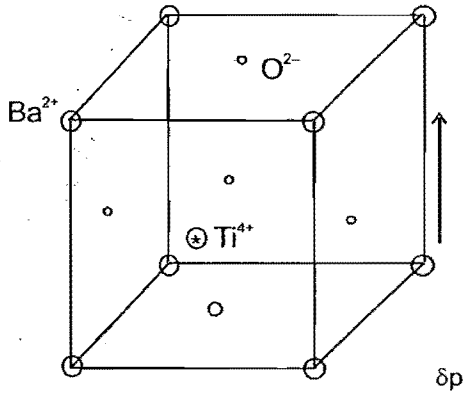
$$\text{or } k^{L} = \frac{\text{Mechanical energy converted to electrical energy}}{\text{Input of Mechanical energy}}$$

Ferroelectric Crystal:

Certain Crystal are the occurrence of spontaneous polarization in certain Crystal such as Barium Titanate ($BaTiO_3$) . Ferroelectric Crystal have a parmanent polarization p as a result of spontaneous polarization
The direction of P can be defined but the application of an external field.

Pyroelectric Crystal:

This material is a polar dielectric (such as $BaTiO_3$) in which a temp change & T induces a proportional change Δp in the polarization that is $\Delta p = p\Delta T$, where p is pyroelectric coefficient of the Crystal



$p = \frac{dp}{dT}$ where p = pyrolectric coeff.

$\delta p = \epsilon_o (\epsilon_o - 1)\delta E$ used as Infrared detectors

$p \neq \epsilon_o (\epsilon_r - 1)E$ rather $\Delta p = \epsilon_o (\epsilon_r - 1)\Delta E$

Δp normal to the plates changes the stored charge which is of relevance.

Example: The electronic polarizability of the Ar atom is 1.7×10^{-14} Fm^2. What is the static dielectric constant of solid Ar (below 84 K) if its density is 1.8 gcm^{-3}.

Soln. $\epsilon_r = 1 + \frac{N\alpha_e}{\epsilon_o}$ where $N = \frac{N_A d}{Mat}$ $\Rightarrow \frac{6.02 \times 10^{23} \times 1.8}{39.95} = 2.71 \times 10^{22}$

$$\therefore \epsilon_r = 1 + \frac{\left(2.71 \times 10^{28}\right)\left(1.7 \times 10^{-40}\right)}{\left(8.85 \times 10^{-12}\right)} = 1.52$$

Using Clausius Mosotti equation $\epsilon_r = \frac{1 + \frac{2N\alpha_e}{3\epsilon_o}}{1 - \frac{N\alpha_e}{3\epsilon_o}} = 1.63$

Example: Consider a pure Si Crystal that has $\epsilon_r = 11.9$

(a) What is the electronic polarizability due to valence electron per Si atom (if one could portion the observed Crystal polarization to Individual atoms)?

(b) Suppose that a Si Crystal sample is electroded on opposite faces and has a voltage applied across it by how much is the local field greater than the applied field?

(c) What is the Reasonant frequency of corresponding $N/v = 5 \times 10^{28}$ m^{-3}.

Soln. (a) $\alpha_e = \frac{3\epsilon_o}{N}\frac{(\epsilon_r - 1)}{(\epsilon_r + 2)} = \frac{3\left(8.85 \times 10^{-12}\right)}{5 \times 10^{28}}\frac{(11.9 - 1)}{(11.9 + 2)} = 4.17 \times 10^{-40} Fm^2$

(b) local field is $E_{loc} = E + \frac{P}{3\epsilon_o}$ $\Rightarrow P = X_e \epsilon_o E = (\epsilon_r - 1)\epsilon_0 E$

$E_{loc} = E + \frac{1}{3}(\epsilon_r - 1)E$ $\Rightarrow \frac{E_{loc}}{E} = \frac{1}{3}(\epsilon_r + 2) = 4.63$

(c) Since Polarization is due to valence electrons and there are four for Si atom, we can

$$\text{Use } W_o = \left(\frac{Z_e^2}{m_e \alpha_e}\right)^{1/2} = \left[\frac{4\left(1.6\times10^{-19}\right)^2}{\left(9.1\times10^{-31}\right)\left(4.17\times10^{-14}\right)}\right]^{1/2} = 1.65\times10^{16}\,\text{rad s}^{-1}, \quad \text{For } \frac{\omega_o}{2\pi} = 2.6\times10^{15}\text{Hz}$$

Example: Consider the CsCl Crystal which has one CS^{-1} Cl^- pair per unit cell and a lattice parametre a of 0.412 nm. The electronic polarizalilty of Cs^+ and Cl^- ions is 3.45×10^{-40} Fm^2 and 3.40×10^{-40} Fm^2 and 3.40×10^{-40} Fm^{-2} respectively, and the mean Ionic polarizability per ion pair is 6×10^{-40} Em^2. What is the dielectric constant at low frequencies and that at optical frequencies.

Soln. The CsCl structure has our cation Cs^+ and one anion (Cl^-) in the unit cell.

Give lattice parameters $a = 0.41\times10^{19}$ m, Number of ions per unit volume Ni is $1/a^3$.

$$Ni = \frac{1}{\left(0.412\times10^{-9}\right)^3} = 1.43\times10^{28}\,m^{-3}$$

also concentration of Cations and Anions

$$\text{now } \frac{\epsilon_r - 1}{\epsilon_0 + 2} = \frac{1}{3\epsilon_0}\left[N_i\alpha_e\left(CS^+\right) + Ni\alpha_e\left(Cl^-\right) + N_i\alpha_i\right]$$

(At low freq.) $\epsilon_r = 7.56$

(At high freq. optical freq.) ionic polarization in two sluggs

$$\frac{\epsilon_r - 1}{\epsilon_0 + 2} = \frac{1}{3\epsilon_0}\left[N_i\alpha_e\left(CS^+\right) + Ni\alpha_e\left(Cl^-\right)\right], \qquad \epsilon_r = 2.71$$

Example: Consider a Piezoelectric sample in the form of a cylinder. Suppose that the piezoelectric coefficient $d = 250\times10^{12}\,mv^{-1}$ and $\epsilon_r = 1000$. The piezoelectric cylinder has a length of 10 mn and a diameter of 3 mm. The spinlc gap is in air and has a break down voltage of about 3.5 kv. What is the force required to spark the gap?

Soln. Induced Polarization T = Stress, $P = dT = \frac{dF}{A}$

Induced polarization leads to induced surface polarization changes given by Q = AP. If C is the capacitance, then the inudced voltage is

$$V = \frac{Q}{C} = \frac{AP}{\frac{\epsilon_o\epsilon_r A}{L}} = \frac{LP}{\epsilon_0\epsilon_r} = \frac{L(dF/A)}{\epsilon_o\epsilon_r} = \frac{dLF}{\epsilon_o\epsilon_r A}$$

$$\therefore F = \frac{\epsilon_o\epsilon_r AV}{dL} = \frac{\left(1000\times8.85\times10^{-12}\right)\times\left(1.5\times10^{-3}\right)^2(3500)}{\left(250\times10^{-12}\right)\left(10\times10^{-3}\right)} = 87.6\text{N}$$

Chapter-10: DEFECTS IN CRYSTALS

We will discuss different types of imperfections or defects in the ideal arrangement of atoms in a crystal. We will see that the presence of a relatively small number of defects have a profound impact on the macroscopic properties of materials, and the control (and intentional introduction) of defects is important in many kinds of material processing

Examples of the relevance of defects in crystals for life in general or materials science in particular: When/if you buy a diamond ring, it is mostly the number and type of defects in the diamond crystal that define the amount of money you pay for a given crystal size. It is generation, accumulation, and interaction of defects in different parts of your car that define the mileage on your car when you tow it to the junk-yard. Production of advanced semiconductor devices requires not only a rather perfect Si crystal as starting material, but also involve introduction of specific defects in small areas of the sample. Forging a metal tool introduces defects and increases strength and elasticity of the tool. Note, that in this case the required properties are achieved without changes in composition of the material, but just by manipulating the crystal defects.

The three basic classes of defects in crystals:

- **Point defects (0-Dimension):** atoms missing or in irregular places in the lattice (lattice vacancies, substitutional and interstitial impurities, self-interstitials).
- **Line defects (1-Dimensional):** groups of atoms in irregular positions (e.g. screw and edge dislocations).
- **Planar defects (2-Dimensional):** the interfaces between homogeneous regions of the material (grain boundaries, stacking faults, external surfaces).

Point Defects: Vacancies

A perfect crystal with regular arrangement of atoms cannot exist. There are always defects, and the most common defects are point defects. This is especially true at high temperatures when atoms are frequently and randomly change their positions leaving behind empty lattice sites, called **vacancies.** In most cases diffusion (mass transport by atomic motion) - can only occur because of vacancies.

How many vacancies are there? The higher is the temperature, more often atoms are jumping from one equilibrium position to another and larger number of vacancies can be found in a crystal. Actually, the number of vacancies, N_v, increases exponentially with the absolute temperature, T, and can be estimated using the equation (Boltzmann Distribution):

$$N_v = N_s \exp\left(-\frac{E_v}{k_B T}\right)$$

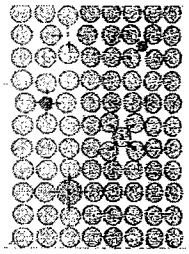
Where N_s is the number of regular lattice sites, k is the Boltzmann constant, and E_v is the energy needed to form a vacant lattice site in a perfect crystal. Using this simple equation we can estimate that at room temperature in copper there is one vacancy pet 10^{15} lattice atoms, whereas at high temperature, just below the melting point there is one vacancy for every 10,000 atoms. These are the lower end estimations, a large numbers of additional vacancies can be introduced in a growth process or as a result of further treatment (plastic deformation, quenching from high temperature to the ambient one, etc.).

More on Point Defects:

Interstitials – atoms that are squeezed in between regular lattice sites. If the interstitial atom is of the same species as the lattice atoms, it is called self-interstitial. Creation of a self-interstitial causes a substantial distortions in the surrounding lattice and costs more energy as compared to the energy for creation of a vacancy ($E_i > E_v$) and, under equilibrium conditions, self-interstitials are present in lower concentrations than vacancies. Foreign, usually smaller atoms (carbon, nitrogen, hydrogen, oxygen) are called interstitial impurities. They introduce less distortion to the lattice and are more common in real materials and more mobile. If the foreign atom atom replaces or substitutes for a matrix atom, it is called a substitutional impurity.

As shown in the schematic drawing, all point defects introduce local distortions to the lattice, and due to these distortions they can feel each other (interact) and feel external stresses. The external stresses or stresses from a larger defects that we will consider next can give a directionality to an otherwise random jumps of atoms. In particular, a pressure gradient results in a flux of vacancies in the direction towards a compressed region of the sample.

- For equilibrium minimum Gibbs free energy G at constant T and P
- A certain concentration of vacancy lowers the free energy of a crystal

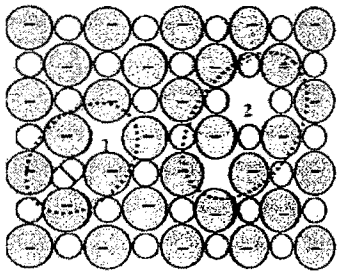


Schematic representation of different point defects in a crystal. (1) Vacancy; (2) self interstitial; (3) interstitial impurity; (4), (5) substitutional impurities. The arrows show the local stresses introduced by the point defects.

In ionic crystals (e.g. table salt – Na^+Cl^-) the bonding is provided by coulombic forces between positively and negatively charged ions. Point defects in ionic crystals are charged as well. The Coulombic forces are very large and any charge imbalance has a very strong tendency to balance itself. To maintain charge neutrality several point defects can be created.

A **Frenkel defect** is a pair of cation (positive ion) vacancy and a cation interstitial. Or it may also be an anion (negative ion) vacancy and anion interstitial. However anions are much larger than cations and it is not easy for an anion interstitial to form.

A **Schottky defect** is a pair of anion and cation vacancies. In both Frenkel and Schottky defects, the pair of point defects stays near each other because of strong coulombic attraction of their opposite charges.



Schematic representation of (1) Frenkel defect (vacancy-interstitial pair) and (2) Schottky defect (a pair of cation and anion vacancies) in an ionic crystal.

Line Defects: Dislocation in Metals

- Edge Dislocation: A portion of an extra plane of atoms
- Screw Dislocation: Helical atomic displacement around a line extending through the crystal
- Mixed Dislocation: Some edge, some screw nature

The interatomic bonds are significantly distorted only in the immediate vicinity of the dislocation line. This area is called the **dislocation core**. Dislocations also create small elastic deformations of the lattice at large distances. To describe the size and the direction of the main lattice distortion caused by a dislocation we should introduce so-called **Burgers vector b**. To find the Burgers vector, we should make a circuit from from atom to atom counting the same number of atomic distances in all directions. If the circuit encloses a dislocation it will not close. The vector that closes the loop is the Burgers vector **b**. Dislocations that have been considered until now have Burgers vector directed perpendicular to the dislocation line. These dislocations are called **edge dislocations**. There is a second basic type of dislocation, called **screw dislocation**. The screw dislocation is parallel to direction in which the crystal is being displaced (Burgers vector is parallel to the dislocation line).

In general, there can be any angle between the Burgers vector **b** (magnitude and the direction of slip) and the line vector **t** (unit vector tangent to the dislocation line).

$\mathbf{b} \perp \mathbf{t} \Rightarrow$ Edge dislocation

$\mathbf{b} \parallel \mathbf{t} \Rightarrow$ Screw dislocation

$\mathbf{b} \perp \mathbf{t}, \mathbf{b} \parallel \mathbf{t} \Rightarrow$ Mixed dislocation

Line energy of a dislocation:

Elastic energy per unit length of a dislocation line ---

$$E = \frac{1}{2}\mu b^2 \quad \text{---} \quad \text{Unit : J m}^{-1}$$

m Shear modulus of the crystal, b Length of the Burgers vector

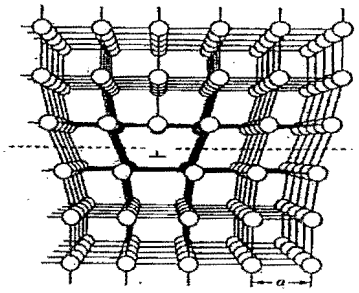


Figure: Edge dislocation

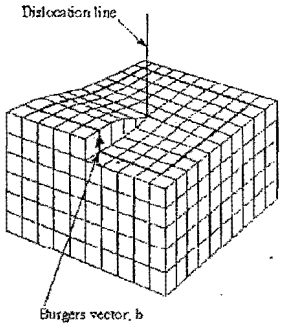
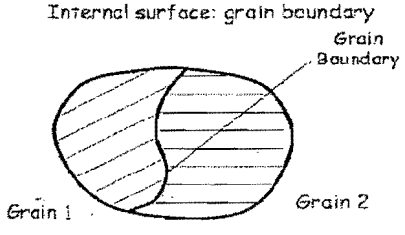


Figure: Screw dislocation

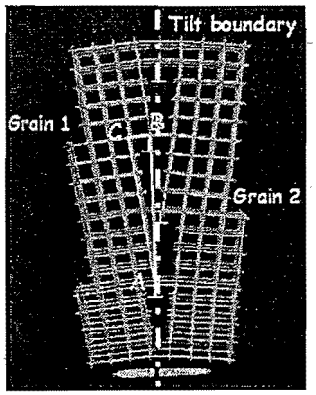
Planar defects: Grain Boundaries:



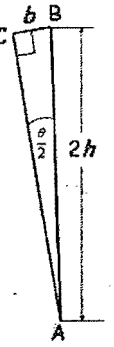
A grain boundary is a boundary between two regions of identical crystal structure but different orientation

Grain Boundary: tilt and twist. One grain orientation can be obtained by rotation of another grain across the grain boundary about an axis through an angle. If the axis of rotation is perpendicular to the boundary plane it is called a twist boundary.

Grain Boundary: low and high angle. One grain orientation can be obtained by rotation of another grain across the grain boundary about an axis through an angle. If the angle of rotation is high, it is called a high angle grain boundary. If the angle of rotation is low it is called a low angle grain boundary.



Edge dislocation model of a small angle tilt boundary



$$\frac{b}{2h} = \sin\frac{\theta}{2}$$

Or approximately

$$\frac{b}{h} = \tan\theta$$

Eqn. 6.7

External surface: Free surface

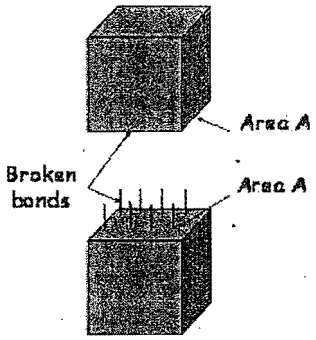
n_A = No. of surface per unit area

n_B = No. of broken bands per surface atom

ε = Bond energy per atom

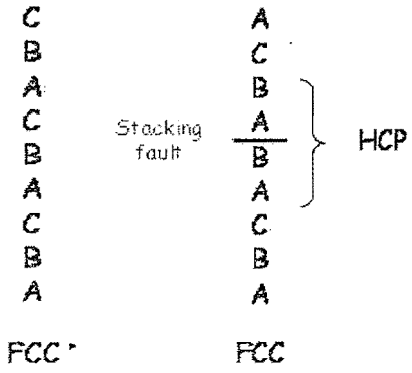
$$\boxed{\gamma = \frac{1}{2} n_A n_B \varepsilon}$$

Surface energy per unit area



If bond are broken over an area A then two free surfaces of a total area 2A is created

Stacking fault



Color centers:

Pure alkali halide crystals are transparent to visible region of spectrum. A color centre is a lattice defect that absorb visible light. Electrons trapped in vacant sites give rise to colour centers.

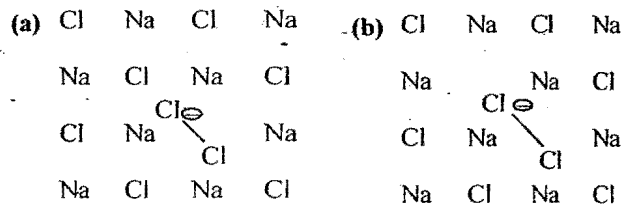
Trapped electrons can be produced by

(i) Irradiation of the sample (ii) Treatment with an electron donor like sodium or potassium vapour

F, H and V centers

- Irradiation can lead to defects where can an electron has been lost or added
- Treatment with alkali metal vapor can lead to excess electrons in material.

Cl	Na-	Cl	Na	Cl	
Na	Cl	Na	Cl	Na	
Cl	Na	e	Na	Cl	F centre– Electron trapped in anion vacancy
Na	Cl	Na	Cl	Na	Example of color center as trapped electron lead to absorption in
Cl	Na	Cl	Na	Cl	visible.



H Center– interstitial Cl atom bonds to lattice Cl^-.
V Center– electron removed from lattice anion site, resulting Cl atom pairs with neighboring Cl^-.

Fig. (a) H-center (b) V-center in NaCl.

M–center consist of two adjacent F-centers.

R-center consist of three adjacent F-centers that mean it is a group of three negative ion vacancies.

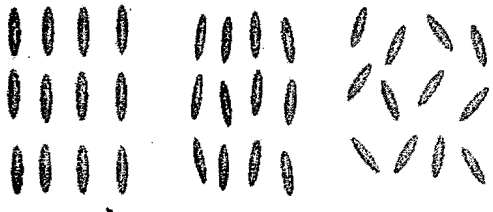
Note:

Mechanism of electrical conductivity in alkali and silver halide crystals is usually the motion of ions and not the motion of electrons. This has been established by comparing the transport of charge with the transport of mass as measured by the material plated out on electrodes in contact with the crystal.

What are Liquid Crystals?

Liquid crystal materials generally have several common characteristics. Among these is a rod-like molecular structure, rigidness of the long axis, and strong *dipoles* and/or easily polarizable substituents.

The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules (*mesogens*) to point along a common axis, called the *director*. This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with liquid crystal state. Note the average alignment of the molecules for each phase in the following diagram.



It is sometimes difficult to determine whether a material is in a crystal or liquid crystal state. Crystalline materials demonstrate long range periodic order in three dimensions. By definition, an isotropic liquid has no orientational

order. Substances that aren't as ordered as a solid, yet have some degree of alignment are properly called liquid crystals.

Liquid crystals can distinguish from isotropic liquid and perfect crystal by an order parameter (S). In an isotropic liquid, order parameter is equal to zero. For a perfect crystal, the order parameter evaluates to one. Typical values for the order parameter of a liquid crystal range between 0.3 and 0.9, with the exact value a function of temperature, as a result of kinetic molecular motion. The tendency of the liquid crystal molecules to point along the director leads to a condition known as anisotropy. This term means that the properties of a material depend on the direction in which they are measured.

Characterizing Liquid Crystals

The following parameters describe the liquid crystalline structure:

- Positional Order
- Orientational Order
- Bond Orientational Order

Positional order:
The extent to which the position of an average molecule or group of molecules shows translational symmetry.

Orientation order:
Measure of the tendency of the molecules to align along the director on a long-range basis. See order parameter.

Bond orientational order:
Describes a line joining the centers of nearest-neighbor molecules without requiring a regular spacing along that line. Thus, a relatively long-range order with respect to the line of centers but only short range positional order along that line.

PHASE TRANSITIONS

(a) First order phase transition: In this transition latent heat (L) is required i.e. entropy (S) is discontinuous at the boundary and volume (V) changes

$L \neq 0,\ \Delta S \neq 0,\ \Delta V \neq 0$

Example: (i) ice $\rightarrow$ water
(ii) water $\rightarrow$ vapour

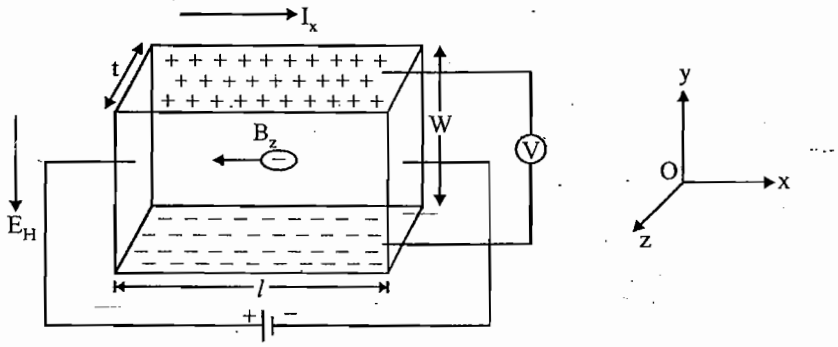
(b) **Second order phase transition:** In this transition

$L = 0,\ \Delta S = 0,\ \Delta V = 0$

Example: (i) Ferromagnet $\rightarrow$ Paramagnet
(ii) Normal conductor $\rightarrow$ Super conductor
(iii) He-I $\rightarrow$ He-II

HALL'S EFFECT:

1. In Metals:



As e^- moving along x direction, as we apply magnetic field B_z in z direction, path of e^- get deflected due to force $\vec{F} = -e(\vec{V} \times \vec{B})$ in downward direction as e^- direction is given by $(\vec{B} \times \vec{V})$ and equal positive charge will be developed on upper side.

Hence if current carrying conductor or semiconductor placed in a perpendicular magnetic field a potential difference is developed both perpendicular to direction of current and direction of magnetic field.

Here E_H is Hall field in $-\hat{y}$ direction.

Now as magnetic force is given by $\vec{F}_m = -e(\vec{V} \times \vec{B})$

But the electric force $\vec{F}_e$ will be opposite to $\vec{F}_m$

i.e. $\vec{F}_e = e\vec{E}$

Then total force will be

$$\vec{F} = eE_H\hat{y} - ev_xB_z\hat{y} = 0$$

$$\boxed{E_H = v_xB_z} \qquad \text{... (1)}$$

$$E_H = -\frac{J_xB_z}{n_e}$$

Now Hall coefficient is given by

$$\boxed{R_H = \frac{E_H}{J_xB_z}}$$

For monovalent metals (Li, Na, K, Rb) R_H = –ve, for divalent metals (B_e, Mg, Ca) etc. R_H = +ve

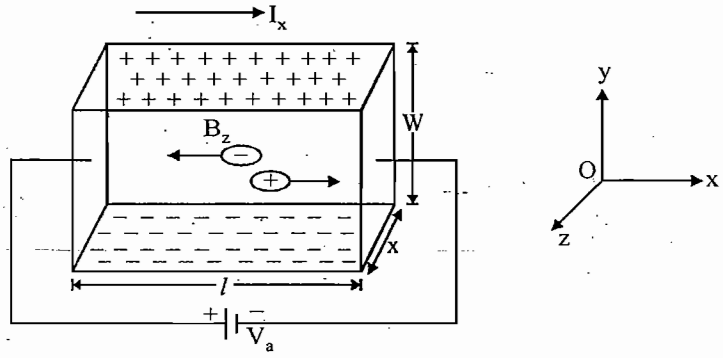
$$R = \frac{V_xB_z}{J_xB_z} = \frac{V_x}{J_x}$$

Here $J_x = -neV_x$

$$\boxed{R_H = -\frac{1}{n_e}} \ m^3/C$$

Hence Hall coefficient depends on concentration of majority charge caries and the sign tells about the type of majority charge carriers.

Case 2. In Semiconductors:



$$E_H = -\frac{J_x B_z}{n_e}$$

$$V_H = E_H W = -\frac{J_x B_z}{n_e} W$$

$$J = \frac{Ix}{wt}$$

$$V_H = -\frac{I_x B_z E_x W}{neWt} = -\frac{I_x B_z E_x}{net} \text{ volt}$$

$V_a = I_x R$ where R is resistance of metal bar.

Q. V_H is double then what will be R_H?
(i) Doubled (ii) Halfed (iii) Same (iv) Cannot determinant

Soln. R_H will remain same because R_H is independent e^- concentration.

Q. If E_x is doubled what will be of R_H?

Soln. If E_x doubled J_x will also get doubled, then R_H or Hall field will be doubled.
To observe hall effect it is necessary that the length must be at least three times of thickness suitable sample for hall effect thin and long.
If this is a semiconducting slab then it will contain both electrons as well as holes.
If semi conductor is intrinsic then e^- and holes will be same in number but effective masses are different and hence. Hall coefficient of is not only depends on e^- and holes concentration. It will depends on μ_H and μ_E.

$$E_H = \frac{B_z J_x (p\mu_h - e\mu_e)}{e(p\mu_h + n\mu_e)^2}$$

$$= \frac{(p^2\mu_{n^2} - nM\mu^2{}_e)}{e(p\mu_h + n\mu_e)^2} \Rightarrow R_H = \frac{n_i\left(\mu_h^2 - \mu_e^2\right)}{n_i e(\mu_h + \mu_e)^2}$$

(i) **For intrinsic $p = n = m$**

$$R_H = \frac{\mu_h - \mu_e}{n_{ie}(\mu_h + \mu_e)} (\mu_e > \mu_h)$$

R_H = –ve

(ii) **For n type: for this $n >> P$**

$$R_H = -\frac{n\mu_e^2}{en^2\mu_e^2} = -\frac{1}{n_e}$$

(iii) **For p-types:**

$$R = \frac{1}{pe}$$

Q. Magnitude of Hall coefficient R_H for semiconductor and metal which one is greater?

Soln. Metal, for a typical metal as $\mu_e > \mu_h$

Q. Can we measure or observe zero value of R_H?

Soln. $R_H = 0$ if $p\mu_h^2 = n\mu_e^2$

Hence we can observe zero value of R_H for a moderately doped semiconductor.